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# Synthesis, catalytic, spectroscopic, fluorescent and coordination properties of dicyanophenoxy-substituted phthalocyaninates of *d*-metals

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Isomeric phthalonitriles having four terminal cyano-groups are synthesized by means of nucleophilic replacement of 4-nitrophthalonitrile's nitro-group with resorcinol and hydroquinone fragments. Corresponding phthalocyaninates of cobalt, zinc, nickel and copper are obtained based on the compounds. The synthesized metal phthalocyaninates are studied in terms of spectroscopic properties using various organic solvents and additionally organic bases. Synthesized cobalt and zinc phthalocyaninates are found to form stable sandwich-type dimers while reacting with 1,4-diazabicyclo[2.2.2]octane (DABCO). Phthalocyaninates having substituted para-positions form more stable sandwich-type agregates than meta-substituted ones. A stability of molecular complexes of 1:1 composition obeys the following order: Py < Pz < DABCO for all synthesized phthalocyaninates.

**Keywords:** Pthalocyanines, d- metals complexes, synthesis, spectroscopic-luminiscent properties, catalysis, aggregation

# 1. Introduction

Metal phthalocyanines have become widespread as effective elements of optics devices <sup>1,2</sup> and electronic systems <sup>3</sup>, stable dyes and pigments, sensitizers <sup>4</sup> as well as highly selective catalysts <sup>5,6</sup>. Such a wide application range originates from the compounds being specific and unique in properties that is reflected by features of the structure, existence of  $\pi$ -conjugated macrocycle core and easyness of modifying preipheral and non-peripheral substituents. One can fine tune properties of

resulting compounds by varying central metal <sup>7</sup> and peripheral substituents. The most prevalent role of phthalocyanine metal complexes in industry is catalysis where the compounds can effectively and selectively catalyze demercaptanization of oil fractions. To date for purposes mentioned above catalysts <sup>8,9</sup> based on metal phthalocyaninates having aromatic fragments bonded to each other in a harsh way are appllied. Such a bonding deprives a molecule of flexibility working its catalytic activity because of sterical hindrance in coming closer of a substrate and an oxidizer with central metal atom. Extension of the periphery by fragments bonded to each other flexibly is one of ways out <sup>10,11</sup>.

Cyano-substituted phthalocyaninates are of certain interests being precursors for polyphthalocyanine structures covalently bonded through a periphery <sup>12–18</sup>. Such systems are applicable due to nonlinear optical properties of third order <sup>19,20</sup>. One can synthesize both homo- and hetero-polymetal structures by utilizing various central metal atoms. It allows fine selective tuning properties of a resulting material depending on necessity. In addition tetrapyrrolic macroheterocycles are known to be prone to aggregation <sup>21</sup>. Aggregation is a prominent, naturally occurring phenomenon that involves automatic formation of dimers and higher aggregate of various and often complex structures. Aggregation of phthalocyanines proceeds in different ways including with small organic ligands <sup>22</sup>. These applications arise from the MPc conjugated  $\pi$ -system, an ability of central cavity to coordinate various ligands and their chemical and physical stability. MPcs can be tuned for different applications by substituting certain position of the macrocycle.

Aggregation is known to affect catalytic properties of phthalocyaninates dramatically. Extension of the periphery with spatially-flexible substituents can provide disaggregation of the molecules due to sterical factor.

Thus, this work is devoted to the preparation of new phthalocyaninates of cobalt, zinc, copper, and nickel with cyanophenoxyl peripheral fragments. The presence of acceptor cyano groups and oxygen atoms provides a shift in electron density from the macrocycle to the periphery, favoring the occurrence of catalytic reactions, along with the flexible structure of substituents due to the presence of oxygen bridges. Based on the obtained phthalocyaninates with terminal cyano groups, it is planned to obtain oligo- and polymeric multinuclear phthalocyanine structures.

# **RESULTS AND DISCUSSION**

#### Synthesis of 4,4'-[1,X-phenylenbis(oxy)]diphthalonitriles

4,4'-[1,4-Phenylenbis(oxy)]diphthalonitrile and 4,4'-[1,3-phenylenbis(oxy)]diphthalonitrile were synthesized by nucleophilic replacement of 4-nitrophthalonitrile's (1) nitro-group with corresponding isomers of dihydroxybenzene. The reaction was carried out in anhydrous DMF accompanied with addition of potassium carbonate (Scheme 1). Reaction mixture was being stirred for 48 h under 25°C. The reaction was controlled by means of thin-layer chromatography (SiO<sub>2</sub>)

utilizing ethanol as eluent. In order to extract phthalodinitriles **2** and **3** the reaction mixture was poured into 0.1 M wateralkali solution, the precipitate was filterred off and washed with water. Then the precipitate was washed with water-alkali solution and water until neutral pH. Excess of a solvent was removed under vacuum. Recrystallization of the compounds was performed from ethanol. Yield of compounds **2** and **3** was 65 and 76% respectively.



Scheme 1. Meta- and para- phenylenebisoxy-substituted diphthalonitriles synthesis route

Compounds 2 and 3 were structurally characterized by means of IR, NMR spectroscopies and MALDI-TOF spectrometry. The IR spectra represent the whole set of characteristic vibrations at 2232-2243 cm<sup>-1</sup>  $\nu$ (C=N), 1243-1256 cm<sup>-1</sup>  $\nu$ (Ar–O –Ar), 1389-1597 cm<sup>-1</sup>  $\nu$ (C<sub>ar</sub>=C<sub>ar</sub>), 2850-3065 cm<sup>-1</sup>  $\nu$ (C<sub>ar</sub>–H). Completeness of+ nucleophilic replacement was also being monitored by IR-spectroscopy method. IR spectra of 2 and 3 contain no bands characterizing symmetric (1340-1350 cm<sup>-1</sup>) and asymmetric (1560-1565 cm<sup>-1</sup>) vibrations of nitro-group's N=O bond evidencing compound 1. Additionally, the band at 1243-1256 cm<sup>-1</sup> appears reflecting skeleton vibrations of Ar-O-Ar group resulting from the reaction.

MADLI-TOF mass-spectra of high definition obtained for **2** and **3** represent molecular signals of m/z equal to 362.11 and 362.09 respectively (Supplementary).

Individuality of obtained compounds **2** and **3** is proved by position, quantity and shape of signals found in <sup>1</sup>H and <sup>13</sup>C spectra (Supplementary) as well as by absence of impurities signals. Para-substitution of resulting dinitrile provides notable shift of all signals to weak field compared to corresponding proton signals registered for meta-one in <sup>1</sup>H NMR spectrum. <sup>13</sup>C spectrum in contrary contains negligible shift (about 1.5-2 ppm) to strong field.

Meta-substitution noteworthy yields higher for 11% compared to similar para-substitution most probably due to steric factor. Corresponding phthalocyaninates of d-metal were obtained based on phthalodinitriles **2** and **3**.

### Synthesis of d-metal phthalocyaninates

Synthesis of the phthalocyaninates is carried out by template melting technique utilizing corresponding nitrile and anhydrous acetate of nickel, cobalt, zink or copper under temperature of 190-195 °C for 30 minutes (till complete

crystallization) (**Scheme 2**). Obtained mixture after cooling is replaced on Shotts filter and washed with water and ethanol in order to remove traces of a salt and a nitrile. Chloroform (for Co and Zn complexes) or acetone (for Ni and Cu complexes) are applied in order to extract desired compound and separate it from polyphthalocyanine fractions. The solvent is removed and the complex is purified by means of column chromatography (SiO<sub>2</sub>) utilizing chloroform (Co, Zncomplexes) or chloroform-acetone mixture (10:1, Ni, Cu-complexes) as eluent.



Scheme 2. Synthesis of Co(II), Zn(II), Ni(II), Cu(II) tetrakis-(dicyanophenoxy)phthalocyanines

Compounds **4-11** were identified with help of IR and NMR spectroscopies as well as MALDI-TOF spectrometry. All obtained metal complexes give mass-spectra representing molecular signal while signals of di- and poly-phthalocyanine systems absent (**Fig. 1**).



Fig. 1. MALDI-TOF mass spectra of cobalt (a - 4, b - 5) and zinc (c - 6, d - 7) complexes

Corresponding IR-spectra for 4-11 represent whole set of characteristic bands (Supplementary). Besides, a phthalocyanine metal complex originated from corresponding dinitrile has more intensive band responding to vibrations of C=N group (~ 2232 cm<sup>-1</sup>) that is explained by bigger number of such a groups.

<sup>1</sup>H NMR spectra of the metal complexes has no extraneous signals and spectrum of each set of metal phthalocyaninates has general view (supplementary) accompanied with a signals shift for 0.02-0.03 ppm to weak field according to the following order Cu - Zn - Ni - Co.

Highest yields are reached in case of Co(II) used as central metal, lowest – in case of Cu(II). In general, yield is higher in case of para-substituted molecules compared to meta-substituted ones.

#### Spectroscopic and coordination properties of Co(II) and Zn(II) phthalocyaninates

Zinc and cobalt complexes are the most prospective as materials for catalysts and photocatalysts <sup>23</sup>. This is due to their ability to coordinate additional ligands into fifth and sixth positions resulting in labile molecular complexes. For the beginning all obtained compounds were studied spectroscopically in various solvents (**Table 1**). There was no deviations from the Lambert-Bouguer-Beer law observed upon study of concentration dependence for solutions of the phthalocyaninates in DMSO, Py, acetone and DMF. Absence of the deviations is explained by specific solvation of central metal cation by the chosen solvents. One can conclude the macrocyclic chromophore under such conditions maintains constant. A shape of a spectrum (**Fig. 2**) indicates the chromophore to be monomeric.



Fig. 2. UV-vis spectra of complexes 4 (a) in 1) Py (2.91×10<sup>-6</sup> M), 2) DMF (1.51×10<sup>-5</sup> M), 3) DMSO (2.86×10<sup>-5</sup> M), 4)
Acetone (1.34×10<sup>-6</sup> M), 5) CHCl<sub>3</sub> (4.41×10<sup>-5</sup> M) and 7 (b) in 1) Py (3.32×10<sup>-6</sup> M), 2) DMF (3.31×10<sup>-6</sup> M), 3) DMSO (3.33×10<sup>-6</sup> M), 4) Acetone (3.67×10<sup>-6</sup> M), 5) CHCl<sub>3</sub> (2.91×10<sup>-6</sup> M).

Meta-substituted complexes of Co(II) and Zn(II) exhibit greater values of extinction compared to para-analogues. Moreover, exchange of Co for Zn is accompanied with increasing extinction coefficients. Varying a solvent does not affect the shape of spectrum but shift Q-band bathochromically or hypsochromically (**Fig. 2**). The most significant red shift of the band for CoPc and ZnPc is observed in DMF. The greates blue shift responds to DMSO.

Compound	Me		λ, hm (lgε)						
Compound		DMSO	Ру	Acetone	CHCl <sub>3</sub>	DMF			
4		662	662	664	669	675 (4 48)			
•	Co	(4.03)	(3.99)	(4.42)	(4.48)	0,0 (11.0)			
5	0	663	664	665	673	677 (3.63)			
5		(3.61)	(3.55)	(3.67)	(4.47)	077 (3.03)			
6		679	678	671	679	675			
U		(4.59)	(4.38)	(4.61)	(4.55)	(4.52)			
7	Zn	680	680	673	681	679 (1 22)			
		(4.44)	(4.28)	(4.45)	(4.59)	078 (4.33)			

Table 1. Spectroscopic characteristics of phthalocyanines 4-7 in various organic solvents

Chloroform solutions of CoPc and ZnPc upon reaching  $5.7 \times 10^{-5}$  M concentration and further increase (**Fig. 3**) exhibit deviation from linearity indicating appearance of new macrocyclic form within the solution. The form is supposed to be H-aggregate.



Fig. 3. UV-vis spectrum changes under dilution of Zn(II) phthalocyanie (7) solution in CHCl<sub>3</sub> at concentration range from  $7.32 \times 10^{-5}$  M to  $3.06 \times 10^{-6}$  M. Insertion – the deviations observed from the Lambert-Buger-Beer's law for phthalocyaninates **4** (a), **5** (b), **6** (c), **7** (d) at the concentrations about  $5.7 \times 10^{-5}$  M.

Interaction between phthalocyaninates and ligands has been studied in order to find aggregation type out. Position of Q-band shifts during titration of CoPc and ZnPc chloroform solutions by pyridine. Spectroscopic behavior is changed indicating axial coordination of pyridine by central metal cation. Addition of pyridine to chloroform solution of CoPc1 causes negligible (up to 5 nm) hypsochromic shift of Q-band that could be caused by appearance of association equilibrium due to increasing solvating ability of mixed solvent (chloroform-pyridine) toward macrocycle periphery. Coordination parameters of pyridine are presented in **Table 2**. All studied phthalocyaninates additionally coordinate only one pyridine molecule into axial position of the metal. Values of thermodynamic constants obtained for pyridinate complexes of studied phthalocyanines (**Table 2**) indicates their low stability.

			•	
	~~~	lgK <sub>s</sub>	/	8
		Ру	Pz	DABCO
Compound	М			
		MPc·L	$(MPc_2 \cdot L_2)_3$	$MPc_2 \cdot L_3$
4		2.67	2.51	4.75
5	Co	2.47	2.73	4.71
6	Zn	2.39	2.48	4.74
7	2.11	2.42	2.87	4.67

 Table 2. Thermodinamical parameters of phthalocyanines complexes 4-7 formation with pyridine and characteristics of pyrazine and DABCO aggrerates stability

Exchange of pyridine with pyrazine used for titration causes significant decrease of Q-band intensity, its bathochromic shift and widening (**Fig. 4**). Titration curve consists of two steps (supplementary). The first step corresponds to bonding between pyrazine molecule and phthalocyanine macrocycle forming 1:1 complex. Higher concentration of pyrazine contributes complexation of molecular complexes resulting in an aggregate of general composition  $(MPc_2L_2)_n$ . Bathochromic shift of Q-band is most probably explained by displacement of macrocycles' dipole moments relative to each

other (aggregation type is close to J-dimers). Bant-Frech calculation results n equal to 3. A stability of such aggregates is to be determined in first by sterical factor of peripheral substituents.



Fig. 4. Spectroscopic changes under tittration of cobalt phthalocyanine (5) solution by pyrazine solution (0.22 M) in CHCl<sub>3</sub>.
Insertion – Bent-French line of phthalocyanines 4 (a), 5 (b), 6 (c), 7(d).

In contrast to pyrazine titration of chloroform solutions of CoPc and ZnPc by DABCO results in hypsochromic shift up to 10 nm. Figure 5 provides parallel disposition of macrocyclic molecules being part of an H-aggregates. The following equilibria occurs upon titration by DABCO:

 $MPc+DABCO \longleftrightarrow MPc \cdot DABCO+ DABCO \bigoplus DABCO \cdot MPc \cdot DABCO$  $MPc \cdot DABCO + MPc \cdot (DABCO)_2 \longleftrightarrow (MPc)_2 \cdot (DABCO)_3$ 



Fig. 5. Spectroscopic changes under titration of cobalt phthalocyanine (5) (7.32×10<sup>-5</sup> M) solution by DABCO solution (0.22 M) in CHCl<sub>3</sub>. Insertion – Bent-French line of phthalocyanines 4 (a), 5 (b), 6 (c), 7(d).

Composition of complexes calculated for every step of titration proves equilibria described above. The first step is coordination of one or two DABCO molecules. Molecular complexes are accumulating till certain concentration when starting to interact with each other forming sandwich-type dimers. Final composition of the complex is MPc:L 2:3. In this way, in contrast to pyrazine forming coordination oligomers consisting of macrocyclic molecules linked through ligand bridge DABCO provides formation of dimeric structures. A stability of dimeric structures containing DABCO is mush higher compared to aggregates with pyrazine (**Table 2**).

	Со		Zn		Cu		Ni	
Subst.	k <sub>obs</sub>	χ, %	$k_{ m obs}$	χ, %	k <sub>obs</sub>	χ, %	k <sub>obs</sub>	χ, %
m-	19.4	34	6.5	14	6.8	9	3.4	7
p-	16.8	36	6.8	16	7.4	8	4.9	8

Table 3. Catalytic parameters of complexes 4-11 in DTC oxidation reaction

The liquid-phase oxidation of DTC in the presence of phthalocyaninates synthesized proceeds more selectively than non-catalytic oxidation. The reaction rate of DTC convertion to tetraethylthiuram disulfide increases up to 19 times in the case of CoPc1. The kinetic curves for all the compounds studied are linear and obey the first-order kinetic equation. The data of **Table 3** show the range of catalytic activity of the compplexes synthesized is as follows: CoPc (m-) > CoPc (p-) > CuPc (p-)  $\geq$  CuPc (m-)  $\geq$  ZnPc (p-)  $\geq$  ZnPc (m-) > NiPc (p-) > NiPc (m-). As expected, cobalt phthalocyaninates are the most active in the series due to the larger partially uncompensated charge on the central metal cation in the macroring. Nickel phthalocyaninates turned out to be the most catalyt i cally disadvantageous due to the high coordination saturation of the bonds between the metal and the macrocycle, which leads to a low ability to coordinate additional axial ligands. Unexpectedly close activity was shown by complexes of copper and zinc, which in this case is obviously associated with the steric and electronic effects of peripheral substituents, which are exerted on the macrocyclic core. A correlation is observed between a series of catalytic activity of the phthalocyaninates obtained and the stability of their 1 : 1 molecular complexes (**Table 2**), which indirectly confirms the course of the oxidation of DTC by the coordination mechanism.

In the phthalocyanine macrocomplex, metals have four bonds with a ligand, namely, two coordination and two covalent ones. Due to the specificity of the electronic structure of the macrocyclic ligand and the presence of aligned  $\pi$ -conjugation in it, all metal-ligand bonds are aligned and they begin to manifest a single nature. Thus, this leads to complete

coordination saturation of nickel in the phthalocyanine macrocomplex<sup>24-25</sup>. Taking into account the coordination mechanism of the manifestation of the catalytic activity of phthalocyanines during the oxidation of sulfur-containing organic substrates<sup>26-29</sup>, considered in this article, the presence of complexation, as well as the formation of a stable triple oxidizingphthalocyanine-substrate complex, is an integral part of the catalytic act. In this regard, the coordination saturation of nickel leads to the possibility of the formation of only a monodentate complex of nickel phthalocyaninate either with an oxidizing agent or with a substrate, the stability of which complicates the process of ligand elimination and electron pair exchange in the ternary complex. In this regard, the probability of the formation of such ternary complexes in the case of nickel phthalocyaninates is less than in the case of complexes with cobalt and copper, which is a key factor affecting the cat activity of these complexes in the oxidation reaction of sulfur-containing compounds. Meanwhile, the close cat activity of cobalt and zinc is quite natural for this reaction due to the fact that in addition to the electric factor, the presence of a successful geometric arrangement of metal cations in the metal complex is essential. Due to the Jahn-Teyler effect, a change in the geometry of the structures of cobalt and zinc complexes occurs, which favors the occurrence of the catalytic act on the one hand, but the insufficient amount of partially uncompensated charge on the central metal ion in the case of the zinc complex leads to a decrease in its activity due to a decrease in the likelihood of the formation of a triple complex<sup>30</sup>. Thus, the close activity between the cobalt and zinc complexes can be explained by the fact that, in the case of the zinc complex, the geometric factor is predominant, and in the case of cobalt, the electronic structure factor of the macrocycle.

In the study of the fluorescent properties of complexes 4-7, a number of regularities were revealed (**Table 4**). So, in the general case, during the transition from cobalt complexes to zinc complexes, a regular increase in the fluorescence quantum yields is observed. Meta-substituted analogues of zinc phthalocyaninates show large values of quantum yields compared with para-analogues, which is probably due to steric effects. The study of the fluorescence quantum yields of aggregates of complexes with pyrazine and DABCO showed that, in general, this type of interaction leads to an increase in the fluorescence properties.

System		4	5	6	7
Ру		0.37%	0.00%	4.18%	5.18%
CHCl <sub>3</sub>		0.52%	0.09%	4.23%	6.16%
Pz	Ру	0.03%	0.08%	8.02%	12.27%

Table 4. Quantum yields of free metalcomplexes 4-7 and their aggregates with pyrazine and DABCO in pyridine and

CHCl<sub>3</sub>

	CHCl <sub>3</sub>	0.06%	0.10%	11.56%	15.73%
DABCO	Ру	0.02%	0.01%	5.80%	5.40%
	CHCl <sub>3</sub>	0.17%	0.02%	7.93%	10.49%

Thus, in the study of aggregates with pyrazine, an increase in the fluorescence quantum yields by 1.5–2 orders of magnitude was observed, and in the case of DABCO up to 1.5 times. Finally, during the transition from pyridine to chloroform, an increase in the fluorescence quantum yields of complexes **4–7** was determined.

#### CONCLUSIONS

Isomeric diphthalonitriles were synthesized during the work. Based on the diphthalonitriles corresponding phthalocyaninates of cobalt(II), zinc(II), nickel(II) and copper(II) were obtained. The compounds were isolated, purified and identified. Meta-substitution was found to yield higher compared to para-substitution. Shift of <sup>1</sup>H NMR proton signals to weak field was revealed in Cu – Zn – Ni – Co series. Obtained compounds were spectroscopically studied in various organic media. Meta-substituted metal complexes demonstrates greater values of extinction coefficients. Cobalt and zinc phthalocyaninates being part of chloroform solution were found to form dimeric sandwich-type structures while interacting with DABCO, whereas interaction with pyrazine leads to formation of oligomeric structures close to J-type aggregates.

# EXPERIMENTAL SECTION

#### **Equipment and reagents**

IR spectra were recorded by means of Fourier-IR spectrophotometer Avatar 360 (USA) in 400-4000 cm<sup>-1</sup> frequency range. The samples were obtained by grinding corresponding crystallic compound combined with anhydrous potassium bromide taken in 1 :100 ratio until homogeneous composition followed with tablet pressing. All data presented in the work was gaining in transmission mode.

Electronic absorption spectra were recorded by means of spectrophotometer UNICO 2800 in 300-1100 nm range utilizing quartz cuvettes of optical path length equal to 1 cm.

NMR spectra were recorded by means of «Bruker AVANCE 500» spectrometer (TMS is inner standard) registering <sup>1</sup>H and <sup>13</sup>C nuclei at 500 and 125 MHz frequencies respectively.

Mass-spectra were registered by means of time-of-flight mass-spectrometer «Simadzu Axima Confidence» (MALDITOF MS). Samples of approximately 10<sup>-3</sup> M concentration were stored in tetrahydrofurane and CHCA (alpha-Cyano-4-hydroxycinnamic acid) was used as a matrix.

Purification of the compounds was performed utilizing silica gel 60 (230-400 mesh).

4-Nitrophthalonitrile (99%, «Sigma-Aldrich»), chloroform (99%), Dimethylformamide (DMF) (99%), Dimethylsulfoxide (DMSO) (99%) pyridine (Py) (99%), acetone (99%), resorcinol (98%) hydroquinone (98%, «Sigma-Aldrich»), 1,4-Diazabicyclo[2.2.2]octane (DABCO) (99.5%, «Sigma-Aldrich»), pyrazine (Pz) (99%, «Sigma-Aldrich») were applied without additional purification. Sodium hydroxide, potassium carbonate and acetates of cobalt(II), zinc(II), nickel(II) and copper(II) were purified and dehydrated right before the experiment according to common techniques.

The homogeneity of the products was tested in each step by TLC (SiO<sub>2</sub>).

# The study of catalytic ativity

The experiment carried out using standard Sodium N,N-diethylcarbamodithioate oxidation reaction. The rection involved was carried out in special constructed cell with volume of 650 ml. The standard temperature was maintained 298.15 K with an accuracy of  $\pm 0.05$  K. Air was supplied via microcompressor with a constant rate of 2 1/min.

After the temperature of the reaction mixture becomes constant, solution was mixed, the sample of 2 ml was selected to determine initial concentration and compressor was turned on. The moment of air supply was the beginning of the reaction. Samples of 2 ml were taken at regular intervals during the experiment to determine the current concentration of the DTC.

Method of DTC determination: sample of 2 ml was moved to the flask of 25 ml and 4ml of CuSO4 solution with concentration of 0.08 M was added. It leads to the formation of dark-brown precipitate – the complex of copper with DTC. Then mixture was stirred. After this 5 ml of chloroform and 0.05 ml of 50% acetic acid was added to the resulting solution. Then it was extracted for 1.5 min. The organic layer was moved into a volumetric flask of 25 ml, and the remaining water solution of the Cu-DTC complex was extracted again to improve the accuracy of analysis. Collected solution of copper complex with DTC was diluted to the exact volume. The optical density of the solution was determined at a wavelength of 436 nm. DTC concentration was calculated with help of the known molar extinction coefficient.

Disulfide formation was monitored with FT-IR, 1H NMR, and <sup>13</sup>C NMR spectra. <sup>1</sup>H NMR of DTC to oxidation (500 MHz, D<sub>2</sub>O):  $\delta$  4.34 (m, J = 15 Hz, 4H, CH<sub>2</sub>); 1.39 (t, J = 5 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR of DTC to oxidation (100 MHz):  $\delta$  11.65, 27.50, 49.08, 205.02. IR of DTC to oxidation IR (KBr): v, cm<sup>-1</sup> 2979 (-CH<sub>3</sub>  $v_{as}$ ), 2847 (-CH<sub>2</sub>-  $v_{as}$ ), 1476 (-CH<sub>2</sub>-  $\delta$ ), 1378 (-C-N <sub>st</sub>), 1269 (-C =S <sub>st</sub>), 1075, (d, -C-S).

During oxidation of DTC the formation of diethylcarbamothioylsulfanyl-N,Ndiethylcarbamodithioate (Thiuram E) is observed. <sup>1</sup>H NMR of Thiuram E obtained by DTC oxidation (500 MHz, CDCl<sub>3</sub>):  $\delta$  3.71-3.77 (m, 8H, CH<sub>2</sub>); 1.29-1.23 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR of Thiuram E obtained by DTC oxidation (100 MHz):  $\delta$  10.49, 25.72, 52.04, 51.26, 190.05. IR of Thiuram E obtained by DTC oxidation IR (KBr): v, cm<sup>-1</sup> 2974 (-CH<sub>3</sub>  $v_{as}$ ), 2861 (-CH<sub>2</sub>-  $v_{as}$ ), 1505 (-CH<sub>2</sub>-  $\delta$ ), 1380 (-C-N <sub>st</sub>), 1273 (-C=S <sub>st</sub>), 1143, 995 (-S-S-).

#### Synthesis

#### Synthesis of 4,4'-[1,3-phenylenebis(oxy)]diphthalonitrile (2)

4-Nitrophthalonitrile (1.00 g, 5.77 mmol) and resorcinol (0.32 g, 2.88 mmol) were dissolved in 100 ml of dry DMF. After stirring for 1 h at room temperature, finely ground anhydrous potassium carbonate (0.99 g, 2.5 mmol) was added to the described solution. The reaction mixture was stirred at 25 °C for 48 h and then it was poured into 300 ml of 0.1 M NaOH aqueous solution. The resulting precipitate were filtered off and washed with deionized water (2 × 30 ml), 0.1 M aqueous solution of NaOH (2 × 30 ml) and finally with deionized water (2 × 30 ml) until neutral pH. Obtaining coarse crude crystals were recrystallized form ethanol to remove any residual of reagents. The pure product was obtained as light yellow powder and it was soluble in chloroform, ethanol, and acetone. Yield 0.68 g (65%) mp 190°C. FT-IR: v<sub>max</sub>, cm<sup>-1</sup> 3088, 2917, 2850 (C<sub>ar</sub> – H); 2243 (C≡N); 1586, 1474, 1389 (C<sub>ar</sub> = C<sub>ar</sub>); 1256 (Ar–O–Ar). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ , ppm 7.76 (dd, 2 H, J = 8.6); 7.55 (t, 1 H, J = 8.3); 7.32 (d, 2 H, <sup>4</sup>J = 2.5); 7.29 (dd, 2 H, <sup>4</sup>J = 2.5, <sup>3</sup>J = 8.3); 6.99 (dd, 2 H, <sup>3</sup>J = 8.3, 4J = 2.2)); 6.82 (m, 1 H, <sup>4</sup>J = 2.2). <sup>13</sup>C NMR (100 MHz, Acetone-d<sub>6</sub>):  $\delta$ , ppm 160.66, 155.52, 135.65, 132.35, 122.03, 117.91, 117.66, 115.10, 114.74, 112.85, 109.91. MS (MALDI-TOF): m/z 362.11 [M]<sup>+</sup>, calcd. 363.08.

## Synthesis of 4,4'-[1,4-phenylenebis(oxy)]diphthalonitrile (3)

4-Nitrophthalonitrile (1.00 g, 5.77 mmol) and hydroquinone (0.32 g, 2.88 mmol) were dissolved in 100 ml of dry DMF. After stirring for 1 h at room temperature, finely ground anhydrous potassium carbonate (0.99 g, 2.5 mmol) was added to the described solution. The reaction mixture was stirred at 25 °C for 48 h and then it was poured into 300 ml of 0.1 M NaOH aqueous solution. The resulting precipitate were filtered off and washed with deionized water (2 × 30 ml), 0.1 M aqueous solution of NaOH (2 × 30 ml) and finally with deionized water (2 × 30 ml) until neutral pH. Obtaining coarse crude crystals were recrystallized form ethanol to remove any residual of reagents. The pure product was obtained as light yellow powder and it was soluble in chloroform, ethanol, and acetone. Yield 0.79 g (76%) mp 190°C. FT-IR:  $v_{max}$ , cm<sup>-1</sup> 3065, 2924, 2850 (C<sub>ar</sub> – H); 2232 (C=N); 1597, 1562, 1479 (C<sub>ar</sub> = C<sub>ar</sub>); 1243 (Ar–O–Ar). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ , ppm 8.01 (d, 2 H, J = 8.7); 7.64 (d, 2 H, J = 2.5); 7.48 (dd, 2 H, J = 8.7, 2.6); 7.35 (s, 4 H). <sup>13</sup>C NMR (100 MHz, Acetone-d<sub>6</sub>):  $\delta$ , ppm 158.36, 154.87, 134.99, 122.12, 120.63, 120.09, 116.70, 116.13, 115.67, 107.79. MS (MALDI-TOF): m/z 362.09 [M]<sup>+</sup>, calcd. 363.08.

#### General way to synthesis tetrakis-(dicyanophenoxy)phthlocyaninetes of Co (4, 5), Zn (6, 7), Ni (8, 9) and Cu (10, 11).

A mixture of compound **2** or **3** (0.20 g, 0.55 mmol) and anhydrous salt of corresponding metal (0.13 mmol) were heated in ceramic crucible for 30 min at 195-200°C. Rough purification was performed by filtration of fusion products on the Schott filter with chloroform to remove residual of polymeric phthalocyanines forms. Further, the solvent was evaporated and the filtrate was subjected to purification using column chromatography (SiO<sub>2</sub>; CHCl<sub>3</sub>).

# Co(II) tetrakis-[3-(3,4-dicyanophenoxy)phenoxy]phthalocyaninate (4)

Yield 0.137 g (66 %). FT-IR:  $v_{max}$ , cm<sup>-1</sup> 3037, 2958, 2921, 2847 (C<sub>ar</sub> – H); 2236 (C=N); 1591, 1473, 1405 (C<sub>ar</sub> = C<sub>ar</sub>); 1245 (Ar–O–Ar). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>):  $\delta$ , ppm 7.92 (s, 4 H), 7.91 (s, 4 H), 7.59 (dd, 8 H, J = 8.7, 2.5 Hz), 7.53 (t, 4 H, J = 2.2 Hz), 7.42 (dd, J = 8.3, 2.2 Hz, 4 H), 7.40 (dd, J = 8.4, 2.3, 4 H), 7.05 (dd, J = 8.3, 2.2 Hz, 4 H), 7.03 (dd, J = 8.2, 2.2 Hz, 4 H), 7.00 (s, 4 H). MS (MALDI-TOF): m/z 1508.43 [M]<sup>+</sup>, calcd. 1508.33. Anal. calcd for C<sub>88</sub>H<sub>40</sub>N<sub>16</sub>O<sub>8</sub>Co: C 70.08, H 2.67, N 14.86, O 8.49, Co 3.91; found: C 70.07, H 2.65, N 14.86, O 8.52, Co 3.90.

#### Co(II) tetrakis-[4-(3,4-dicyanophenoxy)phenoxy]phthalocyaninate (5)

Yield 0.143 g (69 %). FT-IR:  $\nu_{max}$ , cm<sup>-1</sup> 3020, 2924, 2853 (C<sub>ar</sub> – H); 2233 (C=N); 1561, 1489 (C<sub>ar</sub> = C<sub>ar</sub>); 1246 (Ar–O–Ar). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>):  $\delta$ , ppm 7.74 (s, 4 H), 7.73 (s, 4 H), 7.29 (d, 8 H), 7.25 (d, J = 2.5 Hz, 4 H), 7.24 (d, J = 2.5 Hz, 4 H), 7.12 (s, 16 H). MS (MALDI-TOF): m/z 1508.16 [M]<sup>+</sup>, calcd. 1508.33. Anal. calcd for C<sub>88</sub>H<sub>40</sub>N<sub>16</sub>O<sub>8</sub>Co: C 70.08, H 2.67, N 14.86, O 8.49, Co 3.91; found: C 70.06, H 2.64, N 14.87, O 8.51, Co 3.93.

### Zn tetrakis-[3-(3,4-dicyanophenoxy)phenoxy]phthalocyaninate (6)

Yield 0.127 g (61 %). FT-IR:  $v_{max}$ , cm<sup>-1</sup> 3081, 2923, 2850 (C<sub>ar</sub> – H); 2232 (C=N); 1591, 1482, 1422 (C<sub>ar</sub> = C<sub>ar</sub>); 1245 (Ar–O–Ar). ). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>):  $\delta$ , ppm 7.90 (s, 4 H), 7.88 (s, 4 H), 7.56 (dd, J = 8.2, 2.1 Hz, 8 H), 7.50 (t, J = 2.2 Hz, 4 H), 7.39 (dd, J = 8.2, 2.1 Hz, 4 H), 7.38 (dd, J = 7.9, 2.2 Hz, 4 H), 7.03 (dd, J = 8.3, 2.3 Hz, 4 H), 7.02 (dd, J = 7.9, 2.1 Hz, 4 H), 6.97 (s, 4 H). MS (MALDI-TOF): m/z 1515.13 [M]<sup>+</sup>, calcd. 1514.77. Anal. calcd for C<sub>88</sub>H<sub>40</sub>N<sub>16</sub>O<sub>8</sub>Zn: C 69.78, H 2.66, N 14.80, O 8.45, Zn 4.32; found: C 69.80, H 2.65, N 14.79, O 8.46, Zn 4.33.

# Zn tetrakis-[4-(3,4-dicyanophenoxy)phenoxy]phthalocyaninate (7)

Yield 0.123 g (59 %). FT-IR:  $v_{max}$ , cm<sup>-1</sup> 3078, 2921, 2853 (C<sub>ar</sub> – H); 2233 (C=N); 1561, 1498, 1482 (C<sub>ar</sub> = C<sub>ar</sub>); 1244 (Ar–O–Ar). 1H NMR (500 MHz, THF-d<sub>8</sub>):  $\delta$ , ppm 7.72 (s, 4 H), 7.70 (s, 4 H), 7.26 (d, J = 2.5 Hz, 8 H), 7.22 (d, J = 2.5 Hz, 4 H), 7.20 (d, J = 2.6 Hz, 4 H), 7.09 (s, 16 H). MS (MALDI-TOF): m/z 1515.09 [M]<sup>+</sup>, calcd. 1514.77. Anal. calcd for C<sub>88</sub>H<sub>40</sub>N<sub>16</sub>O<sub>8</sub>Zn: C 69.78, H 2.66, N 14.80, O 8.45, Zn 4.32; found: C 69.80, H 2.64, N 14.80, O 8.47, Zn 4.34.

# Ni(II) tetrakis-[3-(3,4-dicyanophenoxy)phenoxy]phthalocyaninate (8)

Yield 0.089 g (43 %). FT-IR:  $v_{max}$ , cm<sup>-1</sup> 3069, 2961, 2924, 2853 (C<sub>ar</sub> – H); 2233 (C=N); 1591, 1473, 1412 (C<sub>ar</sub> = C<sub>ar</sub>); 1247 (Ar–O–Ar). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>):  $\delta$ , ppm 7.92 (s, 4 H), 7.90 (s, 4 H), 7.59 (dd, J = 8.1, 2.1 Hz, 8 H), 7.52 (t, J = 2.2 Hz, 4 H), 7.41 (dd, J = 7.9, 2.2 Hz, 4 H), 7.40 (dd, J = 8.0, 2.1 Hz, 4 H), 7.04 (dd, J = 8.2, 2.2 Hz, 4 H), 7.03 (dd, J = 8.1, 2.2 Hz, 4 H), 7.00 (s, 4 H). MS (MALDI-TOF): m/z 1508.06 [M]<sup>+</sup>, calcd. 1508.09. Anal. calcd for C<sub>88</sub>H<sub>40</sub>N<sub>16</sub>O<sub>8</sub>Ni: C 70.09, H 2.67, N 14.86, O 8.49, Ni 3.89; found: C 70.10, H 2.66, N 14.85, O 8.51, Ni 3.90.

## Ni(II) tetrakis-[4-(3,4-dicyanophenoxy)phenoxy]phthalocyaninate (9)

Yield 0.079 g (38 %). FT-IR:  $v_{max}$ , cm<sup>-1</sup> 3072, 2923, 2854 (C<sub>ar</sub> – H); 2231 (C=N); 1490, 1412 (C<sub>ar</sub> = C<sub>ar</sub>); 1236 (Ar–O–Ar). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>):  $\delta$ , ppm 7.73 (s, 4 H), 7.71 (s, 4 H), 7.27 (d, J = 2.5 Hz, 8 H), 7.23 (d, J = 2.5 Hz, 4 H), 7.21 (d, J = 2.6 Hz, 4 H), 7.10 (s, 16 H). MS (MALDI-TOF): m/z 1508.19 [M]<sup>+</sup>, calcd. 1508.09. Anal. calcd for  $C_{88}H_{40}N_{16}O_8Ni$ : C 70.09, H 2.67, N 14.86, O 8.49, Ni 3.89; found: C 70.11, H 2.66, N 14.86, O 8.50, Ni 3.91.

# Cu(II) tetrakis-[3-(3,4-dicyanophenoxy)phenoxy]phthalocyaninate (10)

Yield 0.135 g (65 %). FT-IR:  $v_{max}$ , cm<sup>-1</sup> 3077, 2924, 2854 (C<sub>ar</sub> – H); 2230 (C=N); 1577, 1479, 1420 (C<sub>ar</sub> = C<sub>ar</sub>); 1248 (Ar–O–Ar). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>):  $\delta$ , ppm 7.89 (s, 4 H), 7.87 (s, 4 H), 7.56 (dd, J = 8.1, 2.2 Hz, 8 H), 7.50 (t, J = 2.2 Hz, 4 H), 7.39 (dd, J = 7.9, 2.2 Hz, 4 H), 7.37 (dd, J = 8.1, 2.2 Hz, 4 H), 7.03 (dd, J = 8.2, 2.1 Hz, 4 H), 7.01 (dd, J = 8.0, 2.2 Hz, 4 H), 6.97 (s, 4 H). MS (MALDI-TOF): m/z 1513.15 [M]<sup>+</sup>, calcd. 1512.94. Anal. calcd for C<sub>88</sub>H<sub>40</sub>N<sub>16</sub>O<sub>8</sub>Cu: C 69.86, H 2.67, N 14.81, O 8.46, Cu 4.20; found: C 69.87, H 2.67, N 14.80, O 8.48, Cu 4.18.

### Cu(II) tetrakis-[4-(3,4-dicyanophenoxy)phenoxy]phthalocyaninate (11)

Yield 0.112 g (54 %). FT-IR:  $v_{max}$ , cm<sup>-1</sup> 3077, 2917, 2853 (C<sub>ar</sub> – H); 2233 (C=N); 1562, 1495, 1483 (C<sub>ar</sub> = C<sub>ar</sub>); 1243 (Ar–O–Ar). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>):  $\delta$ , ppm 7.71 (s, 4 H), 7.69 (s, 4 H), 7.25 (d, J = 2.5 Hz, 8 H), 7.21 (d, J = 2.5 Hz, 4 H), 7.19 (d, J = 2.6 Hz, 4 H), 7.08 (s, 16 H). MS (MALDI-TOF): m/z 1513.05 [M]<sup>+,</sup> calcd. 1512.94. Anal. calcd for C<sub>88</sub>H<sub>40</sub>N<sub>16</sub>O<sub>8</sub>Cu: C 69.86, H 2.67, N 14.81, O 8.46, Cu 4.20; found: C 69.88, H 2.65, N 14.82, O 8.47, Cu 4.18.

# Spectroscopic studies

Spectroscopic studies were carried out for isomolar series of solutions. Calculation of stability constant for MePc-L molecular complex formation was carried out based on changes of absorption density of solution in range of Q band.

$$K_{s} = \frac{[nL \cdot CoPc]}{[CoPc] \cdot [L]^{n}}$$
(1)

Equilibrium concentration of molecular complex was calculated as:

$$c_{CoPc-L} = c_{CoPc}^{0} \cdot \frac{(A_0 - A_c)}{(A_0 - A_{\infty})}$$
(2)

where  $c_{MePc\cdot L}$  – equilibrium concentration of molecular complex,  $c_{MePc}^0$  – initial concentration of macrocycle. A<sub>0</sub>, A<sub>c</sub> and A<sub>∞</sub> – initial, equilibrium and final values of solution's optical density of Q band respectively.

Concentration of free ligand was determined according to equation:

$$c_{L} = c_{L}^{0} - c_{CoPc}^{0} \cdot \frac{(A_{0} - A_{c})}{(A_{0} - A_{\infty})}$$
(3)

Taking into account equations 2 and 3 the formula for calculating stability is to be:

$$K_{s} = \frac{\left[ (A_{0} - A_{c}) / (A_{c} - A_{\omega}) \right]}{\left[ c_{L}^{0} - c_{CoPc}^{0} \cdot (A_{0} - A_{c}) / (A_{0} - A_{\omega}) \right]}$$
(4)

The investigation was carried out with excess of ligand relative to the metallophthalocyanine. That is why equilibrium concentration of the ligand is considered to be equal to its initial concentration. It simplifies calculating  $K_s$ :

$$K_{s} = \frac{A_{0} - A_{c}}{(A_{0} - A_{\infty})c_{L}^{0}}$$
(5)

To estimate the number of units of forming sandwich associates the semi-log method of Bent-French by value of the slope of plots was applied

$$\lg\left(\frac{A_0 - A_c}{A_c - A_{\infty}}\right) = f\left(lgc_L\right) \tag{6}$$

where  $c_L$  – equilibrium concentration of axial ligand,  $A_0$ ,  $A_c \lor A_{\infty}$  – initial, equilibrium and final values of solution's optical density respectively

Constants of associate stability (B) were obtained based on EAS data of two wavelengths (before and after the shift) <sup>31</sup> and calculated according to:

$$\beta = \frac{[MPc \cdot L \cdot MPc]}{[MPc \cdot L][MPc]} = \frac{1}{[MPc \cdot L]} \left( \frac{\Delta A_{i,\lambda_1} \Delta A_{0,\lambda_2}}{\Delta A_{0,\lambda_1} \Delta A_{i,\lambda_2}} \right)$$
(7)

where  $\lambda_1$  – initial wavelength,  $\lambda_2$  – wavelength after the shift of absorption maximum,  $\Delta A_0$  – maimal change of ptical density at given wavelength,  $\Delta A_i$  – change of optical density at given wavelength and concentration.

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# REFERENCES

- Zawadzka, A.; P, P.; Strzelecki, J.; Korcala, A.; Arof, A. K.; Sahraoui, B. Impact of Annealing Process on Stacking Orientations and Second Order Nonlinear Optical Properties of Metallophthalocyanine Thin Fi Lms and Nanostructures. *Dye. Pigment.* 2014, 101, 212–220. https://doi.org/10.1016/j.dyepig.2013.09.044.
- (2) Birnbaum, T.; Hahn, T.; Martin, C.; Kortus, J.; Fronk, M.; Lungwitz, F.; Zahn, D. R. T. Optical and Magneto-Optical Properties of Metal Phthalocyanine and Metal Porphyrin Thin Films. J. Phys. Condens. Matter 2014, 26, 104201. https://doi.org/10.1088/0953-8984/26/10/104201.

- (3) Zhang, R.; Xu, B.; Wang, J.; Zhao, J. Binuclear Transition Metal Phthalocyanines with Superior Performance as Electrocatalysts for Lithium / Thionyl Chloride Battery. J. Mater. Res. 2014, 29, 793–800. https://doi.org/10.1557/jmr.2014.48.
- (4) Hartle, M. D.; Sommer, S. K.; Dietrich, S. R.; Pluth, M. D. Chemically Reversible Reactions of Hydrogen Sul Fi de with Metal Phthalocyanines. *Inorg. Chem.* 2014, 6, 7800–7802. https://doi.org/10.1021/ic500664c.
- (5) Saka, E. T.; Çakir, D.; Biyiklioğlu, Z.; Kantekin, H. New Soluble Peripherally Tetra-Substituted Co(II), Fe(II)
   Phthalocyanines: Synthesis, Spectroscopic Characterization and Their Catalytic Activity in Cyclohexene Oxidation.
   *Dye. Pigment.* 2013, 98 (2), 255–262. https://doi.org/10.1016/j.dyepig.2013.02.021.
- (6) Aktas, A.; Acar, I.; Biyiklioglu, Z.; Saka, E. T.; Kantekin, H. Synthesis, Electrochemistry of Metal-Free, Copper, Titanium Phthalocyanines and Investigation of Catalytic Activity of Cobalt, Iron Phthalocyanines on Benzyl Alcohol Oxidation Bearing 4-{2-[3-Trifluoromethyl)Phenoxy]Ethoxy} Groups. *Synth. Met.* 2014, 198, 212–220. https://doi.org/10.1016/j.synthmet.2014.10.022.
- (7) Vannikov, A.; Grishina, A. D.; Gorbunova, Y. G.; Zolotarevskii, V. I.; Krivenko, T. V.; Laryushkin, A. S.; Lapkina, L. A.; Savelev, V. V.; Tsivadze, A. Y. Influence of Heavy Central Atom on Photoelectric, Nonlinear Optical, and Photorefractive Properties of Metal Phthalocyanines. *High Energy Chem.* 2015, 49, 36–43. https://doi.org/10.1134/S0018143915010142.
- (8) Vashurin, A.; Kuzmin, I.; Razumov, M.; Golubchikov, O. Catalytically Active Systems of Cobalt Complexes with Water-Soluble Phthalocyanines. *Macroheterocycles* 2018, *11* (1), 11–20. https://doi.org/10.6060/mhc180168v.
- (9) Vashurin, A. S.; Pukhovskaya, S. G.; Semeikin, A. S.; Golubchikov, O. A. Catalytic Properties of Cobalt Meso -Tetrakis (4-Methylpyridiniumyl) - Porphyrin Tetratosylate in the Oxidation of Sodium Diethyldithiocarbamate. *Macroheterocycles* 2012, 5 (1), 72–75. https://doi.org/10.6060/mhc2012.111251v.
- (10) Erzunov, D. A.; Vashurin, A. S.; Koifman, O. I. Synthesis and Spectral Properties of Isomers of Cobalt Tetrakis(Dicyanophenoxy)Phthalocyaninate. *Russ. Chem. Bull. (Int Ed)* **2018**, 67 (12), 2250–2252.
- Oluwole, D. O.; Yagodin, A. V; Mkhize, N. C.; Sekhosana, K. E. First Example of Nonlinear Optical Materials
   Based on Nanoconjugates of First Example of Nonlinear Optical Materials
   Based on Nanoconjugates of Sandwich
   Phthalocyanines with Quantum Dots. *Chem. A Eur. J.* 2017, 23, 2820–2830.

https://doi.org/10.1002/chem.201604401.

- (12) Yazici, A.; Dalbul, N.; Altindal, A.; Salih, B.; Bekaroglu, O. Partition Coefficient-Lewis Basicity Correlation in Four Dioxycyclobutenedion-Bridged Novel Ball-Type Phthalocyanines. *Synth. Met.* 2016, 212, 25–30. https://doi.org/10.1016/j.synthmet.2015.11.029.
- (13) Wang, K.; Huang, C.; Pan, H.; Kobayashi, N.; Jiang, J. Post-Cyclotetramerization Strategy towards Novel Binuclear Phthalocyanine Dimers. *Inorg. Chem.* 2017, *4*, 110–113. https://doi.org/10.1039/C6QI00408C.
- Bilgin, A.; Mendi, A.; Yildiz, U. Novel Phthalocyanine Polymers with Very Flexible Pentathiatetraethylene Units.
   *Polymer (Guildf).* 2006, 47, 8462–8473. https://doi.org/10.1016/j.polymer.2006.10.018.
- (15) Yazici, A.; Saricicek, B.; Altindal, A.; Salih, B.; Bekaroglu, O. Synthesis and Characterization, Electrical and Gas Sensing Properties of N,N'-Bis(Salicylidene)-1,2-Phenylendiamine Substituted Novel Mono and Ball-Type Metallo Phthalocyanines. *Inorganica Chim. Acta* 2015, 428, 83–92. https://doi.org/10.1016/j.ica.2015.01.027.
- (16) Koudia, M.; Abel, M. Step by Step On-Surface Synthesis: From Manganese Phthalocyanines to Their Polymeric Form. *Chem. Commun.* 2014, *50*, 8565–8567. https://doi.org/10.1039/C4CC02792B.
- (17) Dubinina, T. V; Tomilova, L. G.; Zefirov, N. S. Synthesis of Phthalocyanines with an Extended System of π-Electron Conjugation. *Russ. Chem. Rev.* 2013, 82 (9), 865–895. https://doi.org/10.1070/RC2013v082n09ABEH004353.
- (18) Tolbin, A. Y.; Pushkarev, V. E.; Tomilova, L. G.; Zefirov, N. S. New Approach to the Synthesis of Planar Binuclear Phthalocyanines of Mg, Zn and Rare Earth Elements. *Macroheterocycles* 2010, *3* (1), 30–32.
- (19) Huang, C.; Wang, K.; Sun, J.; Jiang, J. Planar Binuclear Phthalocyanine-Containing Sandwich-Type Rare-Earth Complexes: Synthesis, Spectroscopy, Electrochemistry, and NLO Properties. *Eur. J. Inorg. Chem.* 2014, No. 9, 1546–1551. https://doi.org/10.1002/ejic.201301485.
- (20) Salan, U.; Altindal, A.; Ozkaya, A. R.; Salih, B.; Bekaroglu, O. Photovoltaic and Electrocatalytic Properties of Novel Ball-Type Phthalocyanines Bridged with Four Dicumarol. *Dalt. Trans.* 2012, 41, 5177–5187. https://doi.org/10.1039/c2dt12510b.
- (21) Bankole, O. M.; YIlmaz, Y.; Nyokong, T. Nonlinear Optical Behavior of Alkyne Terminated Phthalocyanines in

Solution and When Embedded in Polysulfone as Thin Films: Effects of Aggregation. *Opt. Mater. (Amst).* **2016**, *51*, 194–202. https://doi.org/10.1016/j.optmat.2015.11.041.

- (22) Vashurin, A.; Filippova, A.; Znoyko, S.; Voronina, A.; Lefedova, O.; Kuzmin, I.; Maizlish, V.; Koifman, O. A New Water-Soluble Sulfonated Cobalt(II) Phthalocyanines: Synthesis, Spectral, Coordination and Catalytic Properties. J. Porphyr. Phthalocyanines 2015, 19 (08), 983–996. https://doi.org/10.1142/S1088424615500753.
- (23) Nesterov, D. S.; Nesterova, O. V; Kopylovich, M. N.; Pombeiro, A. J. L. Pronounced Retention of Stereoconfiguration upon Sp3 C-H Bonds Hydroxylation of Dimethylcyclohexanes and Decahydronaphthalenes with m - CPBA Oxidant and a Co-Phthalocyanine Catalyst. *Mol. Catal.* 2018, 459 (August), 8–15. https://doi.org/10.1016/j.mcat.2018.08.009.
- (24) Leznoff, C. C.; Lever, A. B. P. Phthalocyanines: Properties and Applications. VCN: Weinheim, 1989, 1.
- (25) Berezin, B.D. Coordination compounds of porphyrins and phthalocyanines. Wiley: New York, Toronto; 1981.
- (26) Tyapochkin, E. M.; Kozliak, E.I. Kinetic and binding studies of the thiolate-cobalt tetrasulfophthalocyanine anaerobic reaction as a subset of the Merox process. J. Mol. Cat. A: Chem. 2005, 242, 1–17. https://doi.org/10.1016/j.molcata.2005.07.008.
- (27) Fischer, H.; Schulz-Ekloff, G.; Wohrle, D. Oxidation of Aqueous Sulfide Solutions by Dioxygen Part 11: Catalysis by Soluble and Immobilized Cobalt(II) Phthalocyanines. Chem. Eng. Technol. 1997, 20, 624-632. https://doi.org/10.1002/ceat.270200909.
- (28) Hoffman, M. R.; Hong, A. P. K. CATALYTIC OXIDATION OF REDUCED SULFUR COMPOUNDS BY HOMOGENEOUS AND HETEROGENEOUS Co(II) PHTHALOCYANINE COMPLEXES. Science of The Total Environment. 1987, 64 (1-2), 99-115. https://doi.org/10.1016/0048-9697(87)90125-2.
- (29) Hoffman, M. R.; Lim, B. C. Kinetics and Mechanism of the Oxidation of Sulfide by Oxygen: Catalysis by Homogeneous Metal-Phthalocyanine Complexes. Environmental science and technology. 1979, 13 (11), 1406-1414. https://doi.org/10.1021/es60159a014.
- (30) Sorokin, A. B. Phthalocyanine Metal Complexes in Catalysis. Chem. Rev. 2013, 113 (10), 8152-8191. https://doi.org/10.1021/cr4000072.

(31) Anderson, H. L.; Hunter, C. A.; Meah, M. N.; Sanders, K. M. Thermodynamics of Induced-Fit Binding Inside Polymacrocyclic Porphyrin Hosts. J. Am. Chem. Soc. 1990, 112, 5780–5789. https://doi.org/10.1021/ja00171a017.

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<sup>1</sup>H NMR spectra of ZnPc1 (6)



MALDI-TOF mass spectra of NiPc1 (8)



MALDI-TOF mass spectra of NiPc2 (9)



MALDI-TOF mass spectra of CuPc1 (10)



MALDI-TOF mass spectra of CuPc1 (11)



FT-IR spectra of 4,4'-[1,3-phenylenebis(oxy)]diphthalonitrile (2)



FT-IR spectra of 4,4'-[1,4-phenylenebis(oxy)]diphthalonitrile (3)





FT-IR spectra of ZnPc1 (6)





- d- metal cyanophenoxy-phthalocyaninates were synthesized and characterized;
- Extra- coordination leads to formation of aggregates close to J- and Htypes;
- Fluorescence quantum yields increase under the aggregation processes were found;
- > Cobalt complexes accelerate DTC oxidation reaction up to 19 times.

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