PHYSICAL, CHEMICAL AND CATALYTIC PROPERTIES OF *β*-SUBSTITUTED DERIVATIVES OF TETRAPHENYLPORPHYRIN

Svetlana Pukhovskaya,[a]* Yuliya Ivanova,[b] Dao The Nam,[a] Ilya Kuzmin,[a] Mikhail Razumov,[a] Natalya Litova[a] and Artur Vashurin[a]

Acidic and basic properties of *β* -substituted derivatives of tetraphenylporphyrin are studied. First and second stage ionization constants for ligands investigated are reported. Acidic properties of porphyrins are in good agreement with classical theories about influence of substituent's nature and geometrical structure of macrocycle on their physical and chemical parameters. It is found that porphyrins have catalytic activity in heterogeneous oxidation of N,N-diethylcarbamodithioate.

*Corresponding Authors
    E-Mail: Svetlana.puhovskaya@mail.ru
[a]   Ivanovo State University of Chemistry and Technology, 153000, Russia, Ivanovo, Sheremetevsky ave. 7
[b]   G. A. Krestov Institute of Solution Chemistry of Russian academy of Sciences, Russia, Ivanovo, 153045, Akademicheskaya str. 1

Introduction

Mercaptans and mercaptides present in light oil and associated gas lead to wear of equipment, oil pipelines and damage the environment. The removal of such compounds is crucial for the technology and environment safety, High yield of oxidation product of mercaptans, which have high toxicity and corrosive activity, may be reached while using the tetrapyrrole macroheterocyclic compounds (metal porphyrins and metal phthalocyanines) as catalysts for deodorant oil refinery. Currently, oxidation of C_1-C_4 thiols to disulfides is carried out by air oxygen in presence of alkali with homogeneous and heterogeneous phthalocyanine catalyst. Investigation of central metal ion's influence showed,[1-3] that cobalt complex with disulfonic acid of phthalocyanine (Pc) has the highest catalytic properties. It is found that catalytic activity decreases in the series: CoPc > CuPc > FePc > NiPc > (Cl)SbPc > AlPc > (Cl)AlPc > ZnPc > (Cl)CrPc.[4]

A number of studies showed that the structure of macrocyclic ligand is also important for catalysis along with the nature of metal cation. Thus, catalytic activity of metallophthalocyanines changes significantly and unambiguously on introducing strong electron-withdrawing substituents into macromolecule. Metal complexes of porphyrins are interesting in this case. Introduction of the substituent in the periphery of porphyrin macrocycle leads to increasing influence of the electronic and structural effects on the coordination unit. Besides, the nature of peripheral substituent affects the way in which the heterogeneous catalysts are obtained. However, there is little information about porphyrins in this field with regard to phthalocyanines.[5,6] Therefore, the influence of nature of substituents in porphyrin macrocycle on physical and

chemical properties of the ligand and on catalytic activity of porphyrin cobalt complexes (**PI – PIII**) (Figure 1) are investigated.
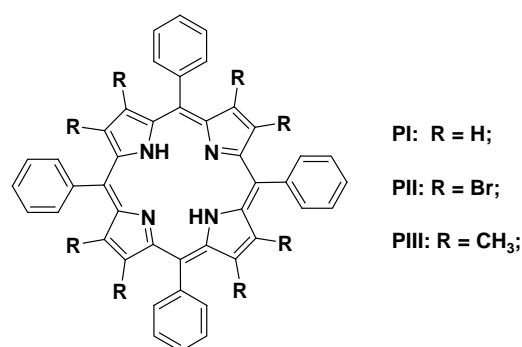
Figure 1. Structure of porphyrins

Experimental

5,10,15,20-Tetraphenylporphyrin (**PI**) was synthesized according to the method described in the literature.[7] UV-vis (chloroform), λ(lg ε): 413(5.60), 513(4.26), 546(3.90), 590(3.70), 650(3.73); ^{1}H NMR (500 MHz, CDCl$_3$, TMS): 8.30 (m, 8 H, phenyl *o*-H), 7.80 (m, 12 H, phenyl *m*- and *p*-H), 8.75 (8H, *β*-C),), -3.75 (s, 2H, NH). Anal. Calcd for $C_{44}H_{30}N_4$: C, 87.12; H, 4.95; N, 7.92. Found: C, 87.15; H, 4.91; N, 7.91. Purification was carried out chromatographically on Al_2O_3 (III degrees of Brockmann activity).

The free-base 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenyl-porphyrin (**PII**) is prepared by bromination reaction of *meso*-tetraphenylporphyrinato copper(II) followed by an acidic demetalation reaction[8,9] 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin is purified chromatographically on Al_2O_3 (II and III degrees of Brockmann activity). Eluent composition: chloroform – benzene. Electron absorption spectra were similar to described in literature.

UV-vis (toluene), λ(lgε): 470 (5.25); 622 (4.10); 738 (3.85). ^{1}H NMR (500 MHz, CDCl$_3$, TMS), 8.21 (m, 8 H, phenyl *o*-H), 7.79 (m, 12 H, phenyl *m*- and *p*-H), -1.65 (bs, 2H, NH). Elemental analysis is consistent with porphyrins without solvent of crystallization. Anal. Calcd for C$_{44}$H$_{22}$N$_4$Br$_8$: C, 42.42; H, 1.78; N, 4.49; Br, 51.30. Found: C, 42.35; H, 1.90; N, 4.40; Br, 51.32.

The free-base 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenyl-porphyrin (**PIII**) is prepared by the literature method.[10] UV-Vis (chloroform), λ (lg ε): 454 (5.27), 555(4.05), 602(3.98), 695(3.67). ^{1}H NMR (500 MHz, CDCl$_3$, TMS), 8.35 (m, 8 H, phenyl *o*-H), 7.93 (m, 12 H, phenyl *m*- and *p*-H), 1,84 (s, 24H, Me), -1.14 (s, 2H, NH). Elemental analysis was consistent with porphyrins without solvent of crystallization. Anal. Calcd for C$_{52}$H$_{46}$N$_4$: C, 86.90; H, 6.40; N, 6.70;. Found: C, 86.91; H, 6.38; N, 6.68.

The purity of the compound was controlled by TLC method on aluminum plates with stacked silica gel F$_{254}$ layer of 0.5 mm thickness ("Merck").

The synthesis of Co(II) porphyrins is carried out according to known method.[11]: 10 mg of porphyrin is dissolved in 50 ml of chloroform to which is added 10 times excess of cobalt acetate. Reaction mixture is heated and boiled for 40-50 minutes. Reaction is controlled by monitoring the change in electron absorption spectrum of the mixture. Degeneration of absorption bands of porphyrin and appearance of absorption bands of its metal complex indicates the completeness of the reaction. After reaction is finished the reaction mixture is cooled and the excess of the salt is removed by water extraction. The cobalt complex is chromatographed on aluminum oxide of III degree of Brockmann activity using chloroform as eluent. The crystalline complex is isolated by precipitation from chloroform.

The dipolar aprotic solvent acetonitrile of high purity (water content is less than 0.03 %) is used as solvent for titration. Initial compounds are in molecular form in this solvent. 1,8-diazabicyclo[5.4,0]undec-7-ene (DBU) is used as deprotonating agent, in acetonitrile DBU has ionization constant of conjugated acid pK_a = 13.2.[12] The reagent is used without additional purification.

Spectrophotometric titration of porphyrin solutions in acetonitrile by DBU solution is carried out on Shimadzu UV-1800 spectrophotometer in a manner described in the literature.[13,14] Error in the determination of the acid ionization constants is not more than 3 %.

Spectra H[1] NMR are recorded on spectrometer «Bruker-500» with an operating frequency of 500 MHz in CDCl$_3$ (internal standard – TMS).

The study of the kinetics of oxidation of sodium N,N-diethylcarbamodithioate (Fig.2) is carried out in specially constructed cell with volume of 650 ml in which 0.3 M solution of N,N-diethylcarbamodithioate (DTC) was loaded with 0.01 g of catalyst. The temperature is maintained 25 ºC within ± 0.05 ºC. The air is fed via microcompressor with constant rate of 2 L min^{-1}. After establishing a constant temperature the solution was mixed and sample of 2 mL was taken to determine initial concentration of DTC, then

compressor was turned on. This moment was taken as the beginning of the reaction. Samples of 2 mL were taken periodically during the experiment to determine current concentration of DTC.
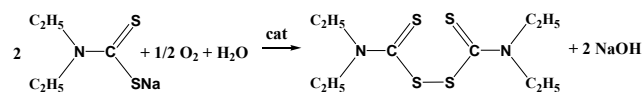
Scheme 1. The reaction of DTC oxidation

The DTC concentration is determined by mixing 4 ml of 0.08 M solution of CuSO$_4$ to 2 mL of the sample solution. A dark-brown precipitate of copper complex is formed. Then 0.005 mL of 50% acetic acid is added and copper complex with DTC is extracted into the chloroform layer. Optical density of solution is determined spectrally at a wavelength of 436 nm. Current concentration of DTC is calculated with help of calibration line.[15]

Under condition of constant oxygen and catalyst concentration and pH of solution the rate of oxidation of DTC is described by first order kinetic equation:

$$\frac{\partial c}{\partial \tau} = -k_{obs} \cdot c \qquad (1)$$

where   *c* is the DTC concentration (M);
          τ is the time (s),
          k_{obs} is the the observed rate constant (s^{-1})

The first order dependence is confirmed by the linear dependence of ln *c* against (τ) and the constancy of the rate constants calculated from the equation.

$$k_{obs} = \frac{\ln \dfrac{c_0}{c}}{\tau} \qquad (2)$$

where c^0 is the initial DTC concentration,
          c is the concentration at time (τ).

It was found in preliminary experiments that non-catalytic oxidation of DTC is very slow (k_{obs} = 1.7 × 10^{-5} s^{-1}).[15]

Activation energies are calculated by using the Arrhenius equation

$$E^{\neq} = 19.1 \left(\frac{T_1 T_2}{T_2 - T_1} \right) \lg \left(\frac{k_2}{k_1} \right) \qquad (3)$$

The conversion was calculated from the equation:

$$\chi = \frac{C^0 - C^{\tau}}{C^0} \qquad (4)$$

where C^0 – initial concentration of DTC,
 C^{τ} – DTC concentration at the current time.

Results and Discussion

A review of literature[16-19] showed that introduction of sterically demanding substituents at the periphery leads to a significantly nonplanar macrocycle conformation Physical and chemical studies[20-23] of the whole series of sterically-disturbed porphyrins brought a direct correlation between the nonplanarity degree of the porphyrin macrocycle and the properties of these compounds.

As shown in our previous work,[24,25] the disturbing of the porphyrin macrocycle planarity leads to decreasing of aromaticity of the molecule and a certain isolation of pyrrole and pyrrolinine fragments. At the same time both basic and acidic properties are enhanced. It suggests that porphyrins with disturbed macrocycle structure will be easily deprotonating in presence of strong bases and hence metal complexation reactions will have higher rates.

Acid properties of porphyrins (**PI** - **PIII**) are studied by spectrophotometric titration method in the system of acetonitrile - 1,8-diazabicyclo[5.4,0]undec-7-ene (5) under 298.15 K. Anionic form of tetraphenylporphyrin (**PI**) was not obtained in this system obviously because of its low acid properties in regards to sterically disturbed derivatives **PII** – **PIII**.

Deprotonation of interior nitrogen atoms of tetrapyrrolic macrocycle proceeds in two steps according to the equations.[26]

$$H_2P \xrightleftharpoons{Ka_1} HP^- + H^+ \qquad (5)$$

$$HP^- \xrightleftharpoons{Ka_2} P^{2-} + H^+ \qquad (6)$$
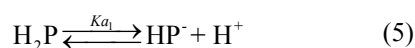
where H_2P; HP^- and P^2 are respectively neutral and deprotonated forms of porphyrin.

Two families of spectral curves are obtained in absorption spectra of compounds II and III during titration. The isosbestic points are obtained and are shown on (Figure 3).
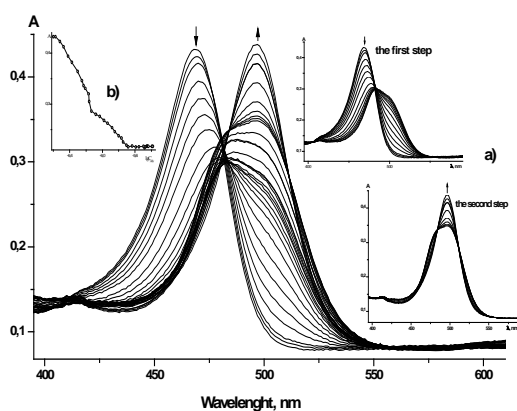
Figure 3. a) Changing in UV-Vis spectra of PII (cPII 2.11×10^{-6} M) in the system AN – DBU (0 ÷ 4.13×10^{-6} M) under 298.15 K, b) Titration curve in the system AN – DBU (0 – 3×10^{-5} M) 298.15 K (λ 449 nm).

The electron absorption spectrum of molecular form (H_2**PII**; λ_{max}, нм (lgε) 470 (5.25), 568 (3.95), 622 (4.10), 738(3.85)) gradually transforms into spectrum of final dianionic form (**PII**$^{2-}$; λ_{max}, нм (lg ε) 497 (5.30), 774 (4.80)) with increasing of titrant concentration (c_{DBU}). For compound **III** respectively: H_2**PIII** 463 (5.15), 548 (3.88), 636 (4.17), 690 (3.63) was transformed into **PIII**$^{2-}$ 439 (4.93), 642 (4.23)

Determination of inflection point coordinate (and corresponding c_{DBU}) on titration curve allows to allocate two regions in absorption spectrum. These regions are likely with regard to the first and second steps of deprotonation, i.e. the formation of mono, and dianionic forms (HP^-, P^{2-}) of compounds (**PII - PIII**). (Figure 4,5) Calculation of current concentrations of deprotonated and molecular forms based on the material balance of the equation showed that the compound **PII** is almost twice deprotonated under the condition of DBU concentration of $3.5 - 4.13 \times 10^{-6}$ M.
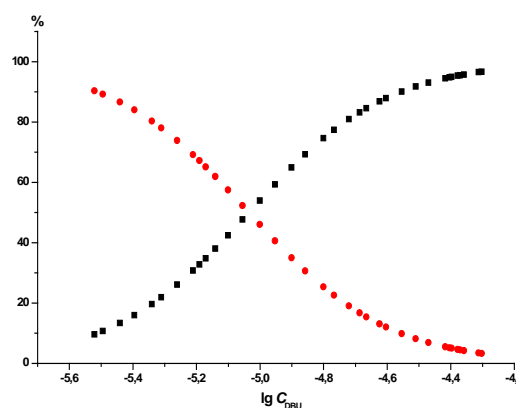
Figure 4. Fractions in % of the doubly deprotonated and the molecular forms in the course of titration for PII

For **PIII**: it transforms to final twice deprotonated form (Figs: 4-5) under the c_{DBU} $3.68 \times 10^{-6} - 3 \times 10^{-5}$ M.

$$c_0 = c_{H_2PII} + c_{PII^{2-}} \qquad (7)$$

The stage deprotonation constants for compounds PII and PIII were calculated according to equations (4) and (5). The values were respectively lgK_1 -6.35; lgK_2 -5.80 и lgK_1 -4.80; lgK_2 -3.95 .

$$\lg K_1 = \lg\left(\frac{[HP^-]}{[H_2P]}\right) + \lg c_{DBU} \qquad (8)$$

$$\lg K_2 = \lg\left(\frac{[P^{2-}]}{[HP^-]}\right) + \lg c_{DBU} \qquad (9)$$

Here are K_1 and K_2 are the constants of acidity of the compound for the first and the second stage, lg(HP^-/H_2P) lg (P^{2-}/HP^-) indicate the ratio for the first and for the second stages of the compounds PII and PIII, lg c_{DBU} is the analytical value of DBU titrant concentration.
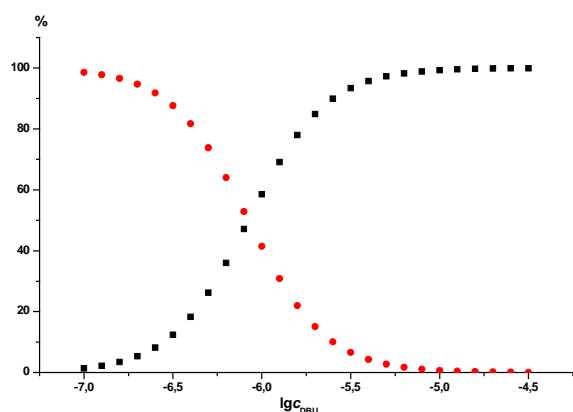
Figure 5. Fractions in % of the doubly deprotonated and the molecular forms in the course of titration for PIII
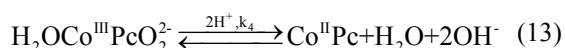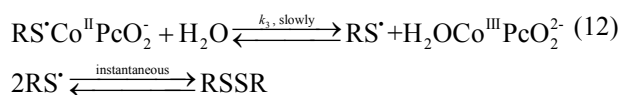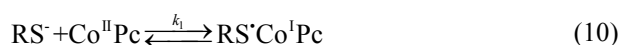
Comparison of values of deprotonation constants showed that in the system acetonitrile DBU 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin is easily deprotonated and has stronger acid properties than 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenylpor-phyrin. Deprotonation of the macrocycle for the first and the second stage differapproximately by two orders.

The (Figure 6) presents kinetic curves of DTC oxidation in presence of cobalt complexes with investigating macrocycles.
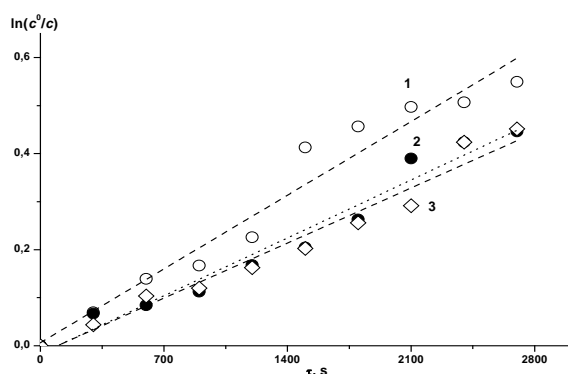
Figure 6. Kinetic curves of DTC oxidation in presence of cobalt complexes with 1) PII, 2) PI, 3) PIII, under 298.15 K, C_{DTC} 3×10^{-3} M.

Kinetic data of DTC oxidation and analysis of known results[27-30] suggest a similar mechanism for homogeneous and heterogeneous conditions. It is known that RS⁻ anion is one stage (equations 10 - 13) in presence of cobalt complexes with tetrapyrrole macroheterocycles like phthalocyanine.

$$RS^- + Co^{II}Pc \underset{}{\overset{k_1}{\rightleftharpoons}} RS^{\cdot}Co^{I}Pc \quad (10)$$

$$RS^{\cdot}Co^{I}Pc + O_2 \underset{}{\overset{k_2}{\rightleftharpoons}} RS^{\cdot}Co^{II}PcO_2^- \quad (11)$$

$$RS^{\cdot}Co^{II}PcO_2^- + H_2O \underset{}{\overset{k_3, \text{slowly}}{\rightleftharpoons}} RS^{\cdot} + H_2OCo^{III}PcO_2^{2-} \quad (12)$$

$$2RS^{\cdot} \underset{}{\overset{\text{instantaneous}}{\rightleftharpoons}} RSSR$$

$$H_2OCo^{III}PcO_2^{2-} \underset{}{\overset{2H^+, k_4}{\rightleftharpoons}} Co^{II}Pc + H_2O + 2OH^- \quad (13)$$

Supposing that the mechanism in equations (10)-(13) is realized in presence of co-porphyrins then introduction of electron-withdrawing substituents would lead to decreasing electron density in coordination center and eases the coordination of the substrate and the formation of triple complex with oxygen $RS^{\cdot} \cdot Co^{II}Pc \cdot O_2^-$.

Table 1. Effective constants of DTC oxidation rate under 298.15 K and activation energies of the process.

Macrocycle	$k_{obs} \times 10^2$, $(s \times g)^{-1}$	$E^{\neq}$, kJ mol^{-1}	χ
CoPI	23.6 ± 0.2	2.37 ± 0.02	64.5
CoPII	59.1 ± 0.3	0.09 ± 0.01	73.6
CoPIII	13.7 ± 0.1	12.93 ± 0.05	67.3

Calculated values of activation energies (Table 1) for this process in presence of investigated porphyrins suggest that there is no diffusion inhibition for the reaction. It supposes that there are two factors affecting the rate of the process: the rate of oxygen supply and its diffusion and the stability of the triple complex which determines the electron effects of peripheral substituents affecting the coordination unit. Under condition of constant rate of oxygen supply the first factor is leveled. It allows determining the influence of macrocyclic molecule periphery on catalytic activity.

Obtained experimental data are in good agreement with classical theories about the influence of substituent's nature, geometrical structure of macrocycle on acid properties of porphyrins. It also shows good similarity with catalytic activity of the porphyrin's cobalt complexes in dithiocarbamic acids oxidation.

Acknowledgments

References

[1]Bricker, J. C., Laricchia, L., *Topics Catal.* **2012**, *55*, 1315.

[2]Joseph, J. K., Jain, S. L., Sain, B., *Ind. Eng. Chem. Res.* **2010**, *49*, 6674.

[3]Das, G., Sain, B., Kumar, S., *Catal. Today* **2012**, *198*, 228.

[4]Zagal, J. H., Griveau, S., Silva, J. F., Nyokong, T., Bedioui, F., *Coord. Chem. Rev.* **2010**, *254*, 2755.

[5]Vashurin, A. S., Pukhovskaya, S. G., Semeikin, A. S., Golubchikov, O. A., *Macroheterocycles* **2012**, *5*,72.

[6]Marfin, Y.S., Vashurin, A.S., Pukhovskaya, S. G., Rumyantsev, E.V., *J. Sol-Gel Sci. Technol.* **2013**, *66*, 306.

[7]Semeikin, A. S., Koifman, O. I., Berezin, B. D., *Chem. Heterocycl. Compd.* **1986**, *22*, 629.

[8]Bhyrappa, P., Krishnan, V., *Inorg. Chem.* **1991**, *30*, 239.

[9]Bhyrappa, P., Nethaji, M., Krishnan, V., *Chem. Lett.* **1993**, 869.

[10]Kuzmin, N. G., Koifman, O. I., *Russ. J. Appl. Chem.* **1988**, *61*, 1426.

[11]Buchler, J. W., *Porphyrins and metalloporphyrins,* Ed. Smith K. M. Amsterdam : Elsevier, **1975**.

[12]Kaljurand, A., Kütt, L., Sooväli, T., Rodima,V., Mäemets, I., Leito, I., Koppel, A., *J. Org. Chem.* **2005**, *70*, 1019.

[13]Ivanova, Yu. B., Sheinin, V. B., Mamardashvili, N. Zh. *Russ. J. Gen. Chem.* **2007**, *77*, 1458.

[14]Ivanova, Yu. B., Churakhina, Yu. I., Mamardashvili, N. Zh., *Russ. J. Gen. Chem.* **2008**, *78*, 673.

[15]Vashurin, A. S., Badaukaite, R. A., Futerman, N. A., Puhovskaya, S. G., Shaposhnikov, G. P., Golubchikov, O. A., *Petr. Chem.* **2013**, *53*, 197.

[16]Senge, M. O., Kalisch, W. W., *Inorg. Chem.* **1997**, *36*, 6103.

[17]Senge, M. O., *In: The Porphyrin Handbook,* Eds. K. M. Kadish, K. M. Smith, R. Guilard. San Diego: Academic Press. **2000**.

[18]Golubchikov, O. A., Pukhovskaya, S. G., Kuvshinova, E. M. *Russ. Chem. Rev.* **2005**, *74*, 249.

[19]D'Souza, F., Zandler, M. E., Tagliatesta, P., Ou, Z., Shao, J., Van Caemelbecke, E., Kadish, K. M., *Inorg. Chem.* **1998**, *37*, 4567.

[20]Comba, P., *Coord. Chem. Rev.* **1993**, *123*, 1.

[21]Pukhovskaya , S. G., Ivanova, Yu. B. , Dao The Nam, Vashurin, A. S., *Russ. J. Phys. Chem. A* **2014**, *88*, 1670.

[22]Ivanova , Yu. B., Chizhova, N. V., Pukhovskaya, S. G., Mamardashvili, N. Zh., *Russ. J. Gen. Chem.* **2014**, *84*, 939.

[23]Fonda, H. N., Gilbert, J. V., Cormier, R. A., Sprague, J. R., Kamioka, K., Connolly, J. S., *J. Phys. Chem.* **1993**, *97*, 7024.

[24]Pukhovskaya, S., Ivanova, Yu., Dao The Nam, Vashurin, A., Golubchikov, O., *J. Porphyrins Phthalocyanines* **2015**, *19*, 858.

[25]Dao The Nam, Ivanova, Yu. B., Puhovskaya, S. G., Kruk, M. M., Syrbu, S. A., *RSC Adv.* **2015**, *5*, 26125.

[26]Berezin, B. D., *Coordination compounds of porphyrins and phthalocyanines,* Wiley, New York, Toronto, **1981.**

[27]Vashurin, A., Maizlish, V., Pukhovskaya, S., Voronina, A., Kuzmin, I., Futerman, N., Golubchikov, O., Koifman, O., *J. Porphyrins Phthalocyanines* **2015**, *19*, 573.

[28] Borisenkova, S. A., *Russ. Petrol. Chem.* **1991**, *31*, 391.

[29]Tyapochkin, E. M., Kozliak, E. I., *J. Mol. Catal. A: Chem.* **2005**, *242*, 1.

[30]Tyapochkin, E. M., Kozliak, E. I., *J. Mol. Catal. A: Chem.* **2003**, *203*, 37.