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Electrochemical route to Co(II) polyporphine

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Abstract

Novel synthetic route towards electroactive films of Co(II) polyporphine has been elaborated. It is based on the electrochemical transformation of the metal-free polyporphine film with replacement of protons inside the macrocycles by Co(II) cations. Compared to the conventional procedure of such ion exchange based on extended thermal treatment of macrocycles in the presence of the saturated solution of the metal salt the developed approach allows one to use dilute solutions of the metal cation at ambient conditions. The resulting Co(II) polyporphine possesses a very high concentration of CoN₄ functional groups which are known as prospective catalysts of various processes.

Keywords: electroactive films, Mg(II) porphine, metalloporphines, electropolymerization, conducting polymer, polymer film coated electrode

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1. Introduction

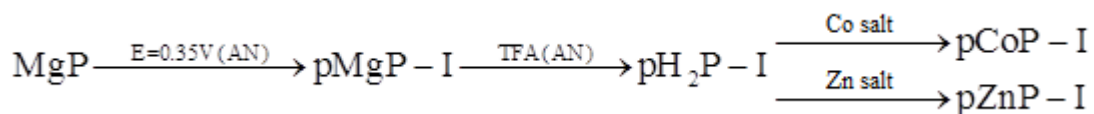
Porphyrin systems are known as basic elements of most important biological structures, including e.g. enzymes and photosynthetic reaction center, which represent now objects of intensive investigations. Owing to the combination of a high chemical stability of the porphyrin macrocycle and its unique physical and chemical properties such materials are widely used in catalysis and electrocatalysis, nonlinear optics, luminescent devices, for solar energy conversion to electricity as well as artificial models of biocatalysts [1,2].

Such prospects have led to numerous attempts of their incorporation into various electroactive materials and coatings. Such modifications of surfaces of various inert electron-conducting substrates (mostly of carbon) have been performed by covalent bonding of metalloporphyrins via various functional groups [3,4], attachment of porphyrins and porphyrin-like heterocycles to the electrode surface owing to adsorption forces, with their subsequent annealing to transform them into "piropolymers" [5] as well as with the use of polymeric coatings composed of polymerizable monomer units containing metalloporphyrin fragments [6-8]. The latter route may lead to polymers where the porphyrinic catalytic center may be located either in the side group as a substituent [7] or inside the principal polymer chain [8].

Efficient synthesis route towards a non-substituted porphyrin, Mg(II) porphine (MgP), has recently been elaborated by J. S. Lindsey et al [9] which has opened the way to an extensive study of this substance. In particular, our team has discovered the possibility of its electropolymerization in acetonitrile (AN) at very low oxidation potentials, resulting in formation of a homopolymer composed of MgP unit linked in their *meso-meso* positions by ordinary bonds, Mg(II) polyporphine of type I (pMgP-I) as a film at the electrode surface [10,11]. Its electrochemical oxidation in the monomer-free solution led to its transformation into another porphine-based polymer having a condensed molecular structure as well as unique optical and redox properties [12]. Compared to the alternative synthesis routes the polyporphine materials in view of no spacers or linkage groups in their structures possess the highest density (per unit mass or surface of the coating) of porphyrin macrocycles which may potentially serve (in combination with a coordinated transition metal cation) as catalytic centers of numerous reactions, including the oxygen reduction process.

Synthesis of such polyporphines containing a coordinated transition metal cation is carried out via a three-stage procedure [13-15]: 1) electrochemical polymerization of MgP at a low potential to grow a pMgP-I film of a controllable thickness at the electrode surface; 2) replacement of Mg(II) cation inside each monomer unit by two protons by ion exchange, thus transforming the layer into the metal-free polyporphine material of type I (pH₂P-I), i.e. having the same molecular structure as pMgP-I; 3) application of the second ion exchange procedure in order to replace protons inside each monomer unit by the desired metal ion, M, also with conservation of the molecular structure of the polymer (pMP-I).

This procedure as a whole has been realized (Scheme 1) for M = Zn(II) [14] and Co(II) [15] by means of treatment of the metal-free polyporphine film, pH₂P-I (demetalated with trifluoroacetic acid, TFA), with concentrated solution of Zn or Co acetate in methanol or dimethylformamide, correspondingly:



Scheme 1. Three-step procedure used to transform the magnesium porphine monomer, MgP, into Zn(II) or Co(II) containing polymetalloporphine, pMP-I.

Synthesis of the Co-containing polyporphine, pCoP-I, is of especial interest in view of a very high concentration of CoN₄ center inside this material. Such a functional group inside molecular porphyrins or phthalocyanines has been widely used at an active electrocatalyst of the oxygen reduction [16] and hydrazine oxidation [17] as well as a sensor element for organic molecules in the gas phase [18] and for various ions in solutions [19].

Among disadvantages of the chemical treatment of the polymer film with concentrated solutions at high temperature (stage 3 of Scheme 1) one can point to the requirement of an enhanced thermal stability of the substrate, contamination of the coating by salt hydrolysis products and a relatively long duration of the procedure (from several tens of minutes to several hours, depending on the thickness of the polyporphine layer).

A novel electrochemical method to replace protons inside the porphine monomer units of the polymer by cobalt cations has been proposed in this work which has allowed us to overcome the above problems.

A novel electrochemical method to replace protons inside the porphine monomer units of the polymer by cobalt cations has been used in this work which has allowed us to overcome the above problems. Its underlying idea is to subject the film-coated electrode to the multi-cycle voltammetric treatment, with the hope that it will result to the replacement of protons inside the central area of the macrocycle by the metal cation from solution. This approach has been successfully employed for various electroactive films, in particular, for substitution of K⁺ or Fe³⁺ cations inside the Prussian Blue films for other transition metal cations [20,21]. Among the films based on macrocycles one can quote the electrochemically performed cobaltation of the metal-free polymers composed of tetraaminophthalocyanine units [22]. At the same time to our best knowledge this method has not been used earlier for the ion exchange inside polymer films based on porphyrin units.

2. Experimental

All electrochemical studies were carried out in three-electrode cell. Several different working electrodes were used: Pt disk (surface area: 0.0078 cm²) or ITO-coated glass plates (surface area: 0.6 cm², for optical measurements) or Pt foil (25 μm thick, for IR spectral measurements). Reference electrode (RE) was composed of Ag wire immersed into 0.01 M AgNO₃ + 0.1 M TBAPF₆ solution in acetonitrile (AN). All values of potential below are given with respect to this RE (its potential is 100 mV more negative than the formal potential of the Fc/Fc⁺ redox couple in 0.1 M TBAPF₆ + AN solution. Platinum wire in contact with 0.1 M TBAPF₆ + AN solution served as counter electrode (CE). Both RE and CE were separated from the working-electrode solution by glassy frits.

Stage 1 of Scheme 1 was performed by means of the potentiostatic oxidation of the monomer, MgP, at 0.35 V [10]. The solution contained about 0.5 mM MgP + 1.5 mM lutidine (Lu) in AN [23]. These conditions ensure deposition of a uniform layer of the Mg(II) polyporphine of type I, pMgP-I, where the neighboring monomer units are linked by *meso-meso* bonds [10,11]. The layer thickness is proportional to the oxidation charge [10], the latter being from 5 to 15 mC/cm². Since the coefficient in this proportionality relation is 9.7 nm·(mC/cm²)⁻¹ [15], the interval of polyporphine layer thicknesses studied here lies between 50 and 150 nm (per vacuum dried material).

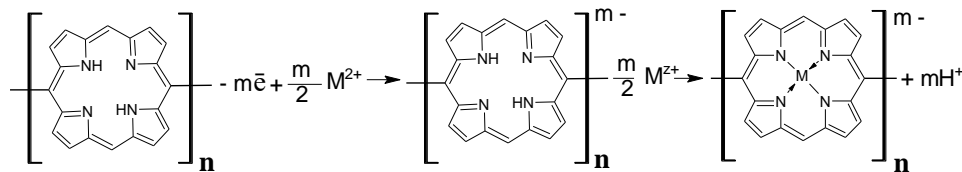
Electrochemical measurements were performed with the use of Elins PI50PRO3 or Autolab PGSTAT 302N potentiostats. Absorption spectra in visible and UV ranges were registered with Lightware II spectrophotometer. IR spectra of films on the Pt foil (after their rinsing by AN and drying in air) were measured ex-situ in the 50-4000 cm⁻¹ range with the use of vacuum Fourier IR spectrometer Bruker Vertex 70v equipped by ATR device with diamante optical element. Registration conditions: 4 cm⁻¹ resolution, signal averaging over 50 scans, vacuum chamber.

Preparative demetalation of the pMgP-I coatings at the electrode surface (stage 2 in Scheme 1) was carried out by their 5-minute contact with deaerated solutions of trifluoroacetic acid (TFA) in AN, their volume ratio being 1 : 50. Then, films were rinsed three times in AN.

Thus obtained metal-free polyporphine films were subject to the metalation procedure (stage 3 in Scheme 1) via the electrochemically-driven ion-exchange method.

3. Results and discussion

The metalation procedure consisted in the electrochemical polarization of the electrode coated by the metal-free polyporphine of type I, pH₂P-I, in contact with solution of the corresponding metal (Co) salt. It had been assumed that the ion exchange with incorporation of the metal cation inside macrocycles of the polymer film could be accelerated owing to the electrostatic attraction of the cation. As it is known, electroactive polymer films which are being charged (positively or negatively) as a response to the corresponding electrode potential are absorbing ions of the opposite charge into the film. Thus, to draw the metal cations from solution into the film one should impose a sufficiently negative potential in order to charge polyporphine (pH₂P-I) molecules. As it is evident from the redox response of this polymer (line 2 in Fig. 3 of Ref [15]) it is charged negatively within the potential range from - 1.1 V to - 1.8 V. Therefore, it is the potential range where one may expect the metal cation absorption by the film, with its further exchange with protons of porphine units (Scheme 2).



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Scheme 2. Co(II) incorporation into the free-base polyporphine, pH₂P-I: electroreduction of the polymer followed by central ion replacement (expected way of electrochemical metalation).

Practical realization of this approach required to carry out the search of the optimal conditions: choice of the solvent, of the Co(II) salt and of the background electrolyte. These components of the system were to satisfy the necessary conditions: sufficient solubility of the salt and sufficiently high conductivity of the solution as well as the absence of side chemical and electrochemical reactions (hydrolysis, cathodic metal deposition, anodic anion oxidation, oxidation or reduction of the solvent) within the required potential range. Such tests were performed by means of studies of the electrochemical stability windows of various Co salts in such organic solvents which should not undergo irreversible transformations within the required potential range with accumulation of insoluble products on the electrode surface, see Fig.1.

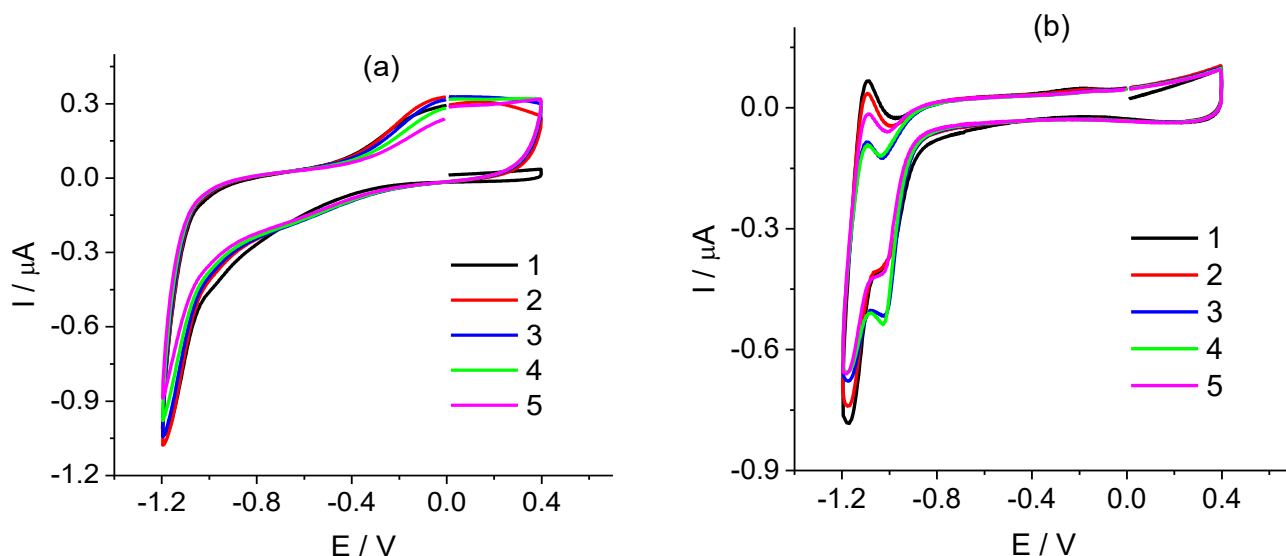


Fig. 1. Cyclic voltammograms (5 cycles) of Pt (a) and glassy carbon (b) electrodes in contact with 0.5 mM $\text{Co}(\text{ClO}_4)_2 + 0.1 \text{ M TBAPF}_6$ in AN. Scan rate: 100 mV/s.

The electrical quantities I , i and E should be written in italics in Figures and text.

MV: quantities on the axes should be written as: E / V or $I / \mu\text{A}$ or $I(Q_{\text{tot}})^{-1} / \text{A C}^{-1}$

As a result of such studies Co(II) perchlorate in $\text{TBAPF}_6 + \text{AN}$ was selected as the solution for the polyporphine metalation. This system allowed us to attain the potential range of the onset of the negative charging of the $\text{pH}_2\text{P-I}$ film (-1.2 V), with no observation of electrochemical reactions leading to insoluble products.

Our procedure applied for metalation of metal-free polyporphine of type I, $\text{pH}_2\text{P-I}$, is based on the exposure of the film-coated electrode to a sufficiently high negative potential in contact with $\text{Co}(\text{ClO}_4)_2 + \text{AN}$ solution at room temperature. Since the ion exchange should lead to liberation of protons from the polymer to solution a special study has been performed for possible effects due to the presence of proton acceptor, lutidine, in solution.

The polarization regime and the interval of imposed potentials have been chosen experimentally. As the most convenient and express method to control the degree of metalation of the polymer after the treatment we used the CV redox response of the film-coated electrode after its transfer into an electrochemical cell with background solution ($0.1 \text{ M TBAPF}_6 + \text{AN}$) which strongly depends on the central ion in monomer units of the polymer, as it is demonstrated in Fig. 2a. Progressive change of the CV response of the initially metal-free $\text{pH}_2\text{P-I}$ film in the course of its metalation is shown in Fig. 2b.

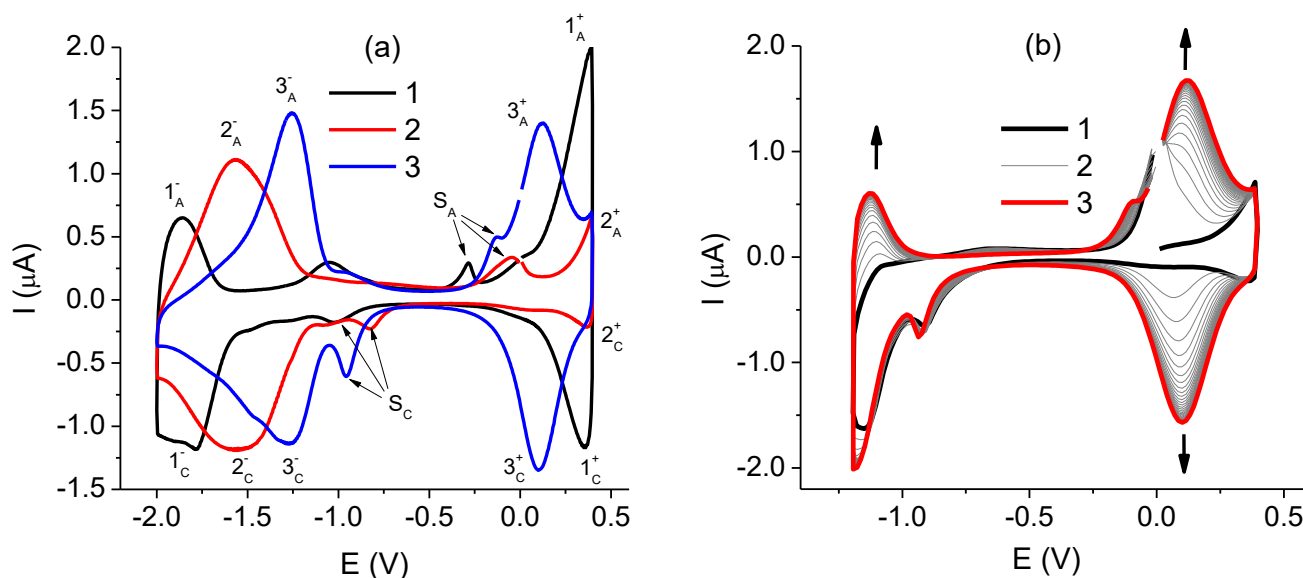


Fig. 2. (a) Cyclic voltammograms of three polyporphine films for Pt disk electrode ($S=0.78 \text{ mm}^2$) in contact with 0.1 M TBAPF_6 in AN; scan rate: 100 mV/s; pMgP-I (line 1), $\text{pH}_2\text{P-I}$ (line 2), pCoP-I (line 3); (b) Series of cyclic voltammograms of Pt disk electrode coated by polyporphine film (which is initially in the $\text{pH}_2\text{P-I}$ state) in the course of its metalation, i.e. in contact with $0.5 \text{ mM Co}(\text{ClO}_4)_2 + 1.5 \text{ mM Lu} + 0.1 \text{ M TBAPF}_6 + \text{AN}$ solution; scan rate: 100 mV/s; cycle 1 (line 1), cycles from 2 to 29 (lines 2), cycle 30 (line 3).

It has been established that it is less efficient to expose the $\text{pH}_2\text{P-I}$ film to a constant negative potential in contact with the metalation solution ($0.5 \text{ mM Co}(\text{ClO}_4)_2 + 0.1 \text{ M TBAPF}_6$ in AN) than to impose several charge-discharge voltammetric cycles (Fig. 3a). Since

the film thicknesses for lines 1-3 in Fig. 3a were different because of various film deposition charges this factor was excluded by division all CV currents by the corresponding deposition charges since the redox response of polyporphine films is proportional to the deposition charge (Fig. 3b).

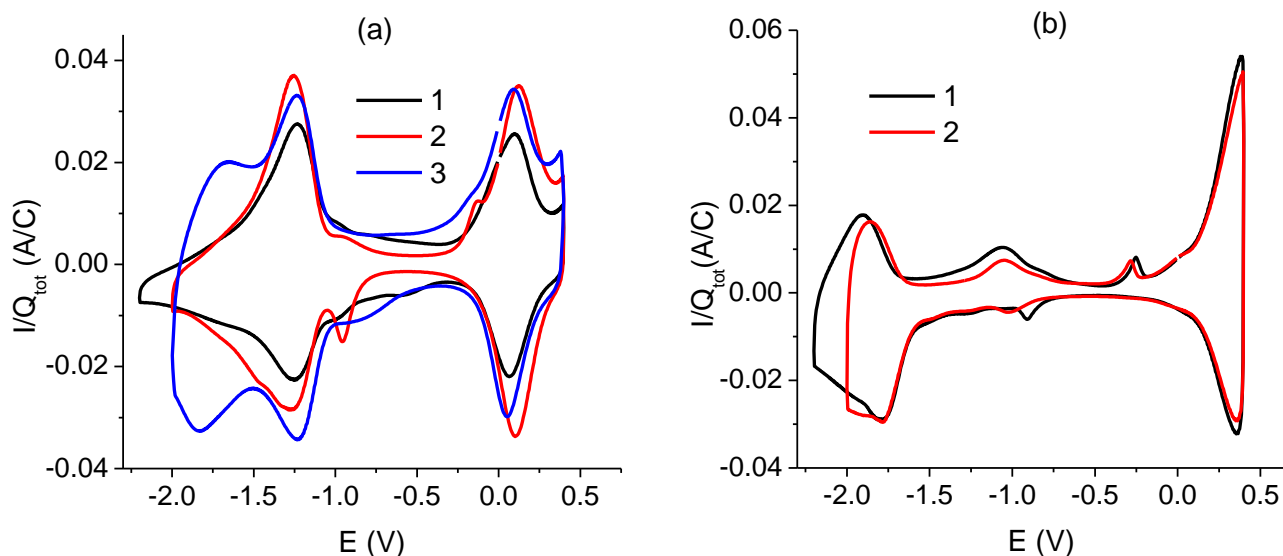


Fig. 3. (a) Stabilized CV response (5th cycles) of polyporphine films at the Pt electrode surface in contact with background solution (0.1 M TBAPF₆ in AN) after their metalation in contact with 0.5 mM Co(ClO₄)₂ + 1.5 mM Lu + 0.1 M TBAPF₆ + AN solution with the use of various procedures: preparative treatment under elevated temperature according to Ref [15] (line 1, charge of the starting pMgP-I film deposition: 9.6 mC/cm²); electrochemical potentiodynamic regime, 30 cycles between 0.4 V and -1.2 V, scan rate: 100 mV/s, overall duration: 24 min (line 2, charge of the starting pMgP-I film deposition: 5.1 mC/cm²); electrochemical potentiostatic regime, -1.2 V for 24 min (line 3, charge of the starting pMgP-I film deposition: 5.1 mC/cm²). All CV currents are divided by the film deposition charge; (b) CV responses (divided by the film deposition charge) of Pt electrode coated with pMgP-I films of different thicknesses in contact with 0.1 M TBAPF₆ + AN solution: film deposition charge was equal to 9.6 mC/cm² (line 1, corresponding to line 1 in Fig. 3a) or 9.6 mC/cm² (line 2, corresponding to lines 2 and 3 in Fig. 3a).

It has been found that the most complete penetration of Co cations into the polyporphine matrix is achieved if the potential is varied between -1.2 V and -0.4 V with the scan rate of 100 mV/s for 30 cycles. The corresponding voltammograms in the course of the metalation procedure (Fig. 2b) show the appearance in the first cycle of redox waves at -1.2 V and +0.1 V and their progressive growth in subsequent cycles, which are characteristic features of the Co(I)/Co(II) and Co(II)/Co(III) transitions, according to data for porphinate complexes of Co [15].

Comparison of the redox responses (in contact with the background solution) of the same polyporphine film before (pH₂P-I) and after (pCoP-I) the metalation procedure demonstrates that their integral intensities are similar. This observation proves that the electric contact between the film and the electrode surface is retained. The completeness of the ion exchange after this metalation process is evidenced by the redox peaks for the initial and final polymer since their potentials are quite different. One can see that the initial redox wave around -1.5 - 1.6 V practically disappeared in the final CV curve, being replaced by characteristic waves due to the redox transitions of Co ions.

One can see in Fig. 2a that the peak potentials of the redox response of the polymer film depend strongly on the central ion. The redox waves for the Mg polyporphine (line 1) are located at - (1.8-1.9) V (couple of waves 1_c⁻/1_a⁺) and expectedly slightly more positive than 0.4 V (onset of waves 1_c⁺/1_a⁺). Demetalation of the polymers (line 2) results in the shift of both waves (couple of waves 2_c⁻/2_a⁺ as well as onset of waves 2_c⁺/2_a⁺) in the positive direction for about 250-300 mV. Both the distance between the peak potentials for the same polymer (2.2-2.3 V) and the shift of the metal-free polymer compared to the Mg one are in good agreement with the corresponding data for molecular porphyrins [24]. All these waves are related to redox processes with participation of the HOMO or LUMO pi-orbitals of the conjugated porphine macrocycle which are affected by the nature of the central ion, Mg(II) or 2 H⁺. The same conclusions are valid for the Zn(II) polyporphine, pZnP-I [14], where the redox transitions of the macrocycle take place at potentials between those for pMgP-I and pH₂P-I polymers.

Insertion of the Co cation into this macrocycle (line 3 in Fig. 2a) changes the situation radically. Its redox waves, 3_c⁻/3_a⁻ and 3_c⁺/3_a⁺, are located at - (1.2-1.3) V and 0.1-0.2 V. The same features are observed for the molecular porphyrins of Co [24]. Therefore, one may conclude that the redox waves in line 3 originate from electronic transitions with participation of the HOMO or LUMO energy levels related dominantly with d-electrons of the central ion.

Two series of experiments have been carried out to study effects of the electrodeposited pMgP-I film thickness and the proton acceptor (Lu) addition in the process of the electrochemical cobalt cation insertion. Films have been deposited in both cases by electropolymerization of MgP at Pt disk electrode with passage of different oxidation charges, 5.1 or 10 or 15.2 mC/cm². Then, the films have been subjected to demetalation (to get metal-free pH₂P-I films) and to electrochemical treatment by 30 potential cycles between 0.4 V and -1.2 V (scan rate: 100 mV/s) in contact with a metalating solution, 0.5 mM Co(ClO₄)₂ + 0.1 M TBAPF₆ in AN for series 1 and 0.5 mM Co(ClO₄)₂ + 1.5 mM Lu + 0.1 M TBAPF₆ in AN for series 2. In all cases the electrochemical cobaltation treatment has led to progressive growth of currents within the potential range corresponding to redox transitions of the porphinate complexes of Co cation (Fig. 2b).

After termination of all three stages of the Co polyporphine synthesis (MgP polymerization resulting in pMgP-I, its demetalation to get pH₂P-I and the Co insertion into the metal-free polymer, Scheme 1) the film-coated electrode was rinsed and transferred to background solution (0.1 M TBAPF₆ in AN) to study its redox properties within the range between 0.4 V and -2.0 V by cyclic

voltammetry. Besides finding the values of peak potentials these data were used to determine the redox charges, Q_- and Q_+ , in the course of the cathodic and anodic potential sweeps, respectively, by integration of the absolute values of the current of the corresponding CV branch within the above potential limits. For both experimental series these charges, Q_- and Q_+ , were practically balanced (their difference was below 5%). This result implies the absence of irreversible transformations of the polymer within this potential range as well as of reactions of solute impurities. The average redox charge for each pMP-I film ($M = \text{Mg}, 2\text{H}$ or Co , Table 1) was found as $Q_{\text{redox}} = 0.5 (Q_+ + Q_-)$. Since the film thickness and its redox charge are proportional to the oxidation charge passed during the pMgP-I film deposition, Q_{tot} , the values of the redox charges in Table are normalized by their division to the corresponding polymerization charge, Q_{tot} .

Comparison of the cobaltation results with the use of the above three methods (Legend to Fig. 3a) is given in Fig. 4 in the form of CV plots (measured after the film-coated electrode transfer into background solution) normalized by division to the corresponding redox charge, Q_{redox} .

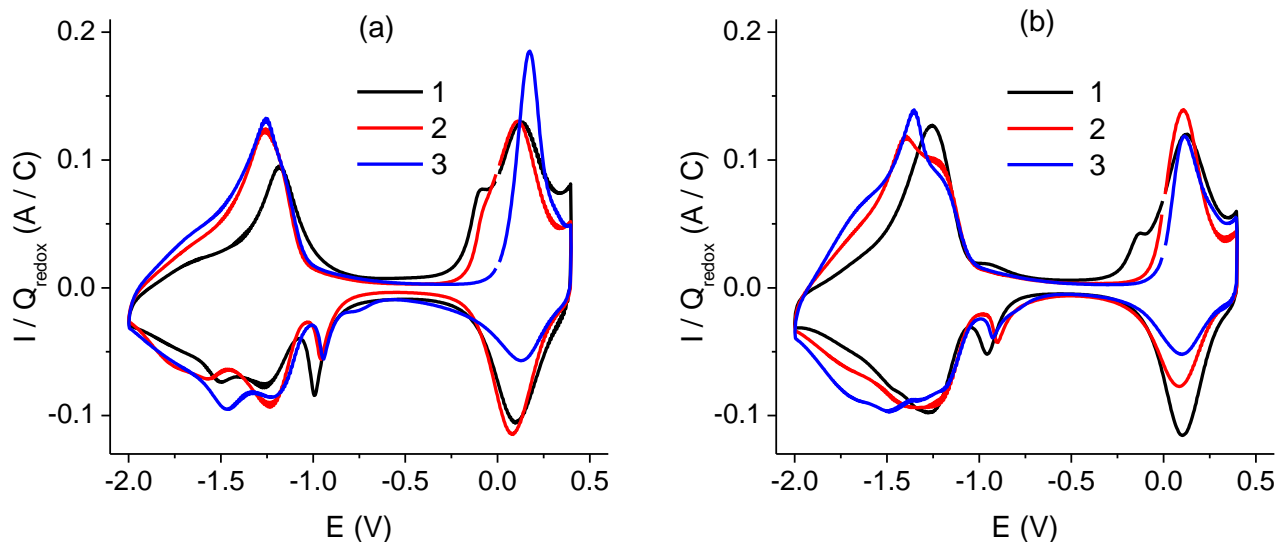


Fig. 4. Stabilized CV responses (5th cycles) of polyporphine films at the Pt disk surface (in contact with background solution, 0.1 M TBAPF₆ in AN) after electrochemical metalation in 0.5 mM Co(ClO₄)₂ + 0.1 M TBAPF₆ in AN (a) or 0.5 mM Co(ClO₄)₂ + 1.5 mM Lu + 0.1 M TBAPF₆ in AN (b). Polymerization charges used for deposition of initial pMgP-I films: 5.1 mC/cm² (lines 1) 10.0 mC/cm² (lines 2) or 15.2 mC/cm² (line 3).

Table 1.

Relation between the oxidation charge, Q_{tot} , used for deposition of initial pMgP-I film and the redox charges of this film, Q_{redox} , for various central ions, Mg(II), 2 H⁺ or Co(II), in the potential range between 0.4 V and - 2.0 V. Scan rate: 100 mV/s.

Cobaltation conditions	$Q_{\text{tot}}, \mu\text{C}$	$Q_{\text{redox}}, \mu\text{C}$			$Q_{\text{redox}}/Q_{\text{tot}}$
	MgP	pMgP-I	pH ₂ P-I	pCoP-I	pCoP-I
without Lu	40	9.7	11.3	12.2	0.31
	78.5	18.9	20.3	26.6	0.34
	120	27.5	29.5	37.8	0.32
with Lu	40	7.9	8.5	11.7	0.29
	78.5	18.2	20.6	26.2	0.33
	120	26.0	29.5	34.6	0.29

Comparison of the corresponding data in Fig. 4a and Fig. 4b as well as in Table 1 allows us to make the conclusion that the presence of the proton acceptor, Lu, in the cobaltation solution does not affect significantly the metalation process. As for the variation of the film thickness within the range of 50 to 150 nm (proportional to the deposition charge, see Fig. 3b and last column of Table 1) the shape of normalized voltammograms (redox peak potentials and intensities of these normalized redox responses) do not depend markedly of this parameter, either. The degree of cobaltation is slightly diminishing with increasing the polymer film thickness, as it is evidenced by residual redox currents in the potential range, - 1.5 V to - 1.7 V, related to remaining metal-free monomer units, H₂P, inside the film. According to Fig. 4b, variation of the polyporphine layer thickness shows the maximal effect on the charging/discharging currents in the potential range from 0 V to 0.2 V corresponding to the Co(II)/Co(III) transition. We attribute it to the insufficiently high electronic conductivity of these films since the polymer matrix is in its non-conducting neutral state within this potential range and the electronic transport takes place via electronic exchanges between neighboring Co(II) and Co(III) centers (hopping mechanism) [15].

Films for characterization of the metalation process via spectral methods were deposited (pMgP-I) on the surface of Pt foil (for IR studies) or of transparent ITO-layer coated glass (for the UV-visible studies), with their subsequent transformation into the metal-free form, pH₂P-I and then into the pCoP-I polymer (Schemes 1 and 2). Thus recorded IR spectra for the Mg(II), metal-free and Co(II) polyporphine films are shown in Fig. 5a. They are compared with the theoretical IR spectra (Fig. 5b) for the corresponding linear

meso-meso bonded trimers, (MgP)₃, (H₂P)₃ and (CoP)₃ (Fig. 5c). This calculation was carried out by means of the hybrid functional density method (B3LYP) with the use of the valent two-exponential basis 6-31G* in the programming complex GAUSSIAN-03 of the computer center of the Institute for Problems of Chemical Physics RAS.

Comparison of these experimental and calculated IR spectra for each polyporphine in Figs. 5a,b reveals a one-to-one correspondence of the changes in the vibrational bands for each transition. In particular, the transition from the Mg(II) system (spectra 1) to the metal-free one (spectra 2) results in both cases a and b in the splitting of the principal band around 1000 cm⁻¹ (A) as well as in appearance of an additional absorption band around 680 cm⁻¹ (B). These effects are induced by lowering the symmetry of the monomer units if a metal cation is replaced by two protons. The second transition related to the Co(II) cation insertion restores the initial symmetry of macrocycle. It is reflected in the IR spectra by lifting out the A band splitting and by disappearance of the B band. This parallelism between the changes in the experimental and theoretical IR spectra represents an additional evidence in favor of the successful replacement of protons inside the macrocycles by Co cations by the proposed metalation procedure. It also shows that no changes of the molecular structure of the polymer takes place in the course of this treatment.

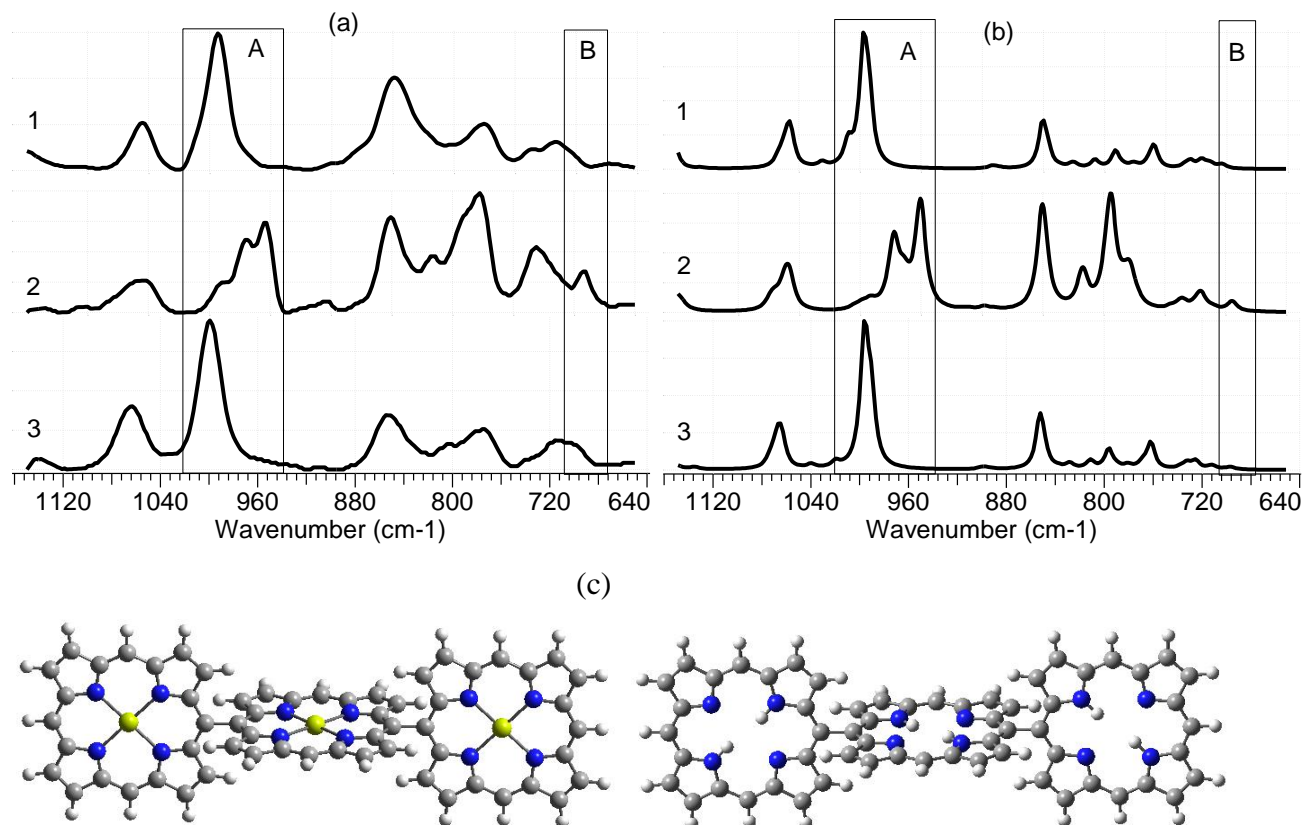


Fig. 5 (a) Central part of the IR spectra of several polyporphine films, pMgP-I (1), pH₂P-I (2) and pCoP-I (3), on Pt foil recorded by ATR method. Electropolymerization charge for pMgP-I: 5 mC/cm²; (b) Calculated vibrational spectra of linear *meso-meso* bonded porphine trimers, (MgP)₃, (H₂P)₃ and (CoP)₃, used as models of the corresponding polymers; (c) optimized structures of trimers with various central ions: metalated systems, (MgP)₃ or (CoP)₃, on the left, metal-free one, (H₂P)₃, on the right.

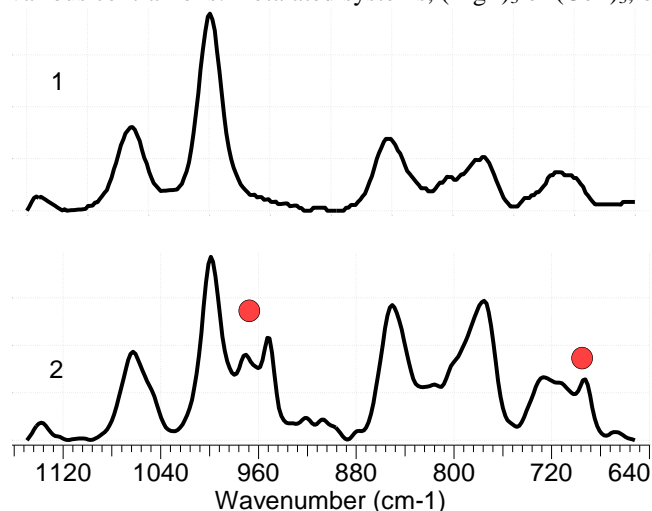


Fig. 6. Central part of the IR spectra of polycobaltporphine films, pCoP-I, of different thicknesses. The films were obtained by ion exchanges from pMgP-I films deposited with passage of two different polymerization charges: 5.1 mC/cm² (spectrum 1) or 15.2 mC/cm² (spectrum 2). Circles for film 2 indicate the absorption bands corresponding to the residual metal-free porphine units inside the polymer layer.

As one can see from data for IR spectra in Fig. 6 the complete cobaltation is only achieved for relatively thin films while a marked fraction of porphine monomer units inside a thicker polymer film remaining non-metalated.

The same macrocycle symmetry factor also plays a significant role in the variation of the optical spectra of both molecular porphines and polyporphines. This assertion is illustrated by absorption spectra of these systems in the UV and visible ranges (Fig. 7). Comparison of such data (lines 1) for the Mg(II) monomer, MgP (Fig. 7a), and its polymer, pMgP-I (Fig. 7b), reveals a very strong broadening towards long-wave lengths of both the Soret (400–500 nm) and Q (500–600 nm) bands for the polymer compared to the monomer (this effect has already been analyzed in Ref [10]). Demetalation of this polymer, pMgP-I, resulting in the metal-free material, pH₂P-I, is accompanied by increase of the number of "steps" in the spectrum and by redistribution of their intensities (line 2 in Fig. 7b). One can see its parallelism with variation of the corresponding monomer spectra (lines 1 and 2 in Fig. 7a), i.e. an increase of the number of Q-bands for H₂P which is expectedly related to its lower symmetry compared that of MgP resulting in a greater number of various electronic energy levels. Insertion of the Co cation into the macrocycle returns the polymeric spectrum to the initial shape (line 3 in Fig. 7b) in conformity with the restoration of the porphine macrocycle symmetry.

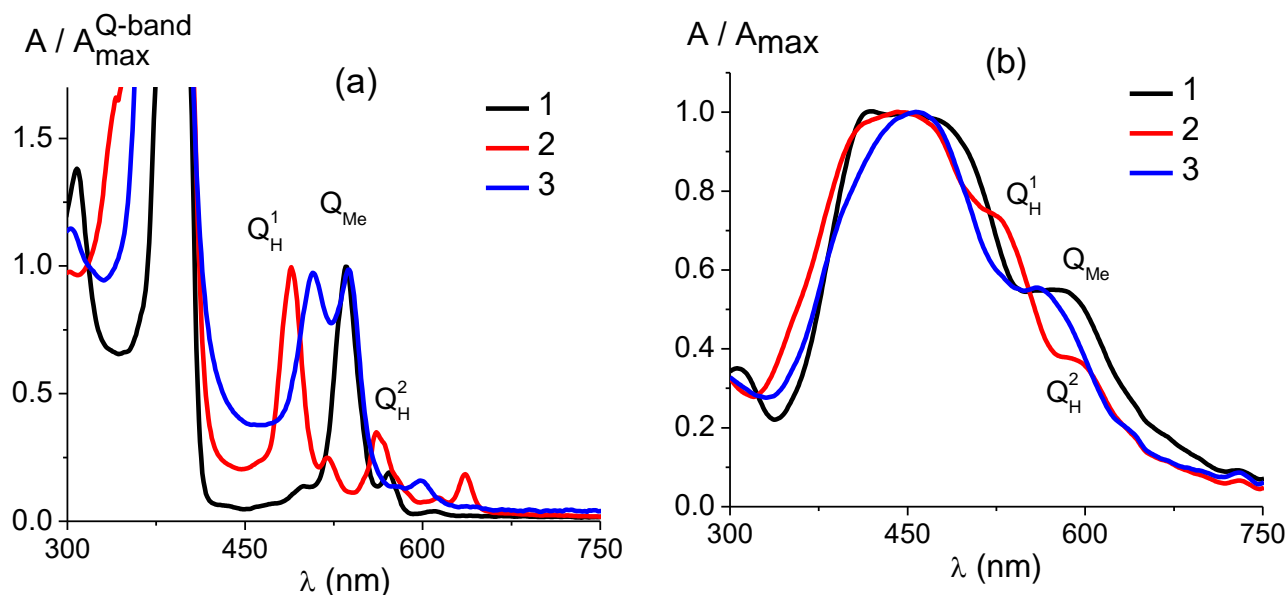


Fig. 7. (a) Absorption spectra of the monomer solutions: MgP (line 1), H₂P (line 2), CoP (line 3); (b) Absorption spectra of polyporphine films (in their neutral states) on the surface of the ITO-coated glass electrodes: pMgP-I (line 1), pH₂P-I (line 2), pCoP-I (line 3); polymerization charge: 5 mC/cm².

4. Conclusions

The evidences discussed in the previous section demonstrate that the proposed electrochemical method for Co cation insertion into the film of the metal-free polyporphine, pH₂P-I, represents an efficient procedure to modify the surface of an inert electron-conductive substrate by a high concentration of the CoN₄ catalytic centers, without application of the long-term thermal treatment or of concentrated metal-salt solutions. These mild synthesis conditions ensure both conservation of the molecular structure of the polymeric matrix and its electric contact with the substrate as well as allow one to avoid contaminations by chemical agents and by their decomposition products.

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References:

- [1] K.S. Suslick, N.A. Rakow, M.E. Kosal, J.H. Chou, The materials chemistry of porphyrins and metalloporphyrins, *J. Porphyr. Phthalocyanines* 4 (2000) 407-413.
- [2] S. Lin, C.S. Diercks, Y.B. Zhang, N. Kornienko, E.M. Nichols, Y. Zhao, A.R. Paris, D. Kim, P. Yang, O.M. Yaghi, C.J. Chang, Covalent organic frameworks comprising cobalt porphyrins for catalytic CO₂ reduction in water, *Science* 349 (2015) 1208–1213.
- [3] R.D. Rocklin, R.W. Murray, Chemically modified carbon electrodes: Part XVII. Metallation of immobilized tetra (aminophenyl) porphyrin with manganese, iron, cobalt, nickel, copper and zinc, and electrochemistry of diprotonated tetraphenylporphyrin, *J. Electroanal. Chem. Interfacial Electrochem.* 100 (1979) 271–282.
- [4] C.P. Jester, R.D. Rocklin, R.W. Murray, Electron Transfer and Axial Coordination Reactions of Cobalt Tetra (Aminophenyl) Porphyrins Covalently Bonded to Carbon Electrodes, *J. Electrochem. Soc.* 127 (1980) 1979-1985.
- [5] M.R. Tarasevich, V.A. Bogdanovskaya, The Surface-modified Carbon Materials for Electrocatalysis, *Russ. Chem. Rev.* 56 (1987) 653-669.
- [6] A. Bettelheim, B.A. White, S.A. Raybuck, R.W. Murray, Electrochemical polymerization of amino-, pyrrole-, and hydroxy-substituted tetraphenylporphyrins, *Inorg. Chem.* 26 (1987) 1009-1017.
- [7] C. Armengaud, P. Moisy, F. Bedioui, J. Devynck, C. Bied-Charreton, Electrochemistry of conducting polypyrrole films containing cobalt porphyrin, *J. Electroanal. Chem. Interfacial Electrochem.* 277 (1990) 197-211.
- [8] M.G. Walter, C.C. Wamser, Synthesis and characterization of electropolymerized porphyrin nanofibers, *MRS Proceedings*. Cambridge University Press 1013 (2007) Z04-07.

- [9] D.K. Dogutan, M. Ptaszek, J.S. Lindsey, Direct synthesis of magnesium porphine via 1-formyldipyrromethane, *J. Org. Chem.* 72 (2007) 5008-5011.
- [10] M.A. Vorotyntsev, D.V. Konev, C.H. Devillers, I. Bezverkhy, O. Heintz, Magnesium(II) polyporphine: The first electron-conducting polymer with directly linked unsubstituted porphyrin units obtained by electrooxidation at a very low potential, *Electrochim. Acta* 55 (2010) 6703–6714.
- [11] D.V. Konev, O.I. Istakova, O.A. Sereda, M.A. Shamraeva, C.H. Devillers, M.A. Vorotyntsev, In situ UV-visible spectroelectrochemistry in the course of oxidative monomer electrolysis, *Electrochim. Acta* 179 (2015) 315-325.
- [12] M.A. Vorotyntsev, D.V. Konev, C.H. Devillers, I. Bezverkhy, O. Heintz, Electroactive polymeric material with condensed structure on the basis of magnesium (II) polyporphine, *Electrochim. Acta* 56 (2011) 3436-3442.
- [13] D.V. Konev, M.A. Vorotyntsev, C.H. Devillers, T.S. Zyubina, A.S. Zyubin, K.V. Lizgina, A.G. Volkov, Synthesis of new polyporphines by replacing central ion in magnesium polyporphine, *Russ. J. Electrochem.* 49 (2013) 753-758.
- [14] D.V. Konev, C.H. Devillers, K.V. Lizgina, T.S. Zyubina, A.S. Zyubin, L.A. Valkova, M.A. Vorotyntsev, Synthesis of new electroactive polymers by ion-exchange replacement of Mg(II) by $2H^+$ or Zn(II) cations inside Mg(II) polyporphine film, with their subsequent electrochemical transformation to condensed-structure materials, *Electrochim. Acta* 122 (2014) 3–10.
- [15] S.D. Rolle, D.V. Konev, C.H. Devillers, K.V. Lizgina, D. Lucas, C. Stern, F. Herbst, M.A. Vorotyntsev, Efficient synthesis of a new electroactive polymer of Co (II) porphine by in-situ replacement of Mg (II) inside Mg (II) polyporphine film, *Electrochim. Acta* 204 (2016) 276-286.
- [16] Y. Ji, Z. Li, S. Wang, G. Xu, X. Yu, Thermal treatment of Co (II) tetracarboxyphenyl porphyrin supported on carbon as an electrocatalyst for oxygen reduction, *Int. J. Hydrogen Energy* 35 (2010) 8117-8121.
- [17] J.E. Bennett, T. Malinski, Conductive polymeric porphyrin films: application in the electrocatalytic oxidation of hydrazine, *Chem. Mater.* 3 (1991) 490-495.
- [18] C. Di Natale, R. Paolesse, M. Burgio, E. Martinelli, G. Pennazza, A. D'Amico, Application of metalloporphyrins-based gas and liquid sensor arrays to the analysis of red wine, *Anal. Chim. Acta* 513 (2004) 49-56.
- [19] R. Paolesse, C. Di Natale, M. Burgio, E. Martinelli, E. Mazzone, G. Palleschi, A. D'Amico, Porphyrin-based array of cross-selective electrodes for analysis of liquid samples, *Sens. Actuators B-Chem.* 95 (2003) 400-405.
- [20] A. Dostal, M. Hermes, F. Scholz, The formation of bilayered nickel-iron, cadmium-iron and cadmium-silver hexacyanoferrates by an electrochemically driven insertion-substitution mechanism, *J. Electroanal. Chem.* 415 (1996) 133-141
- [21] M. Hermes, M. Lovric, M. Hartl, U. Retter, F. Scholz, On the electrochemically driven formation of bilayered systems of solid Prussian-blue-type metal hexacyanoferrates: a model for Prussian blue _ cadmium hexacyanoferrate supported by finite difference simulations, *J. Electroanal. Chem.* 501 (2001) 193–204
- [22] W. J. Todd , F. Bailly , J. Pavez , P. W. Faguy , R. P. Baldwin , R. M. Buchanan, Electrochemically Induced Metallation of Polymeric Phthalocyanines, *J. Am. Chem. Soc.*, 120 (1998) 4887-4888
- [23] D.V. Konev, C.H. Devillers, K.V. Lizgina, V.E. Baulin, M.A. Vorotyntsev, Electropolymerization of non-substituted Mg (II) porphine: Effects of proton acceptor addition, *J. Electroanal. Chem.* 737 (2015) 235-242.
- [24] K. M. Kadish, E. V. Caemelbecke, G. Royal, Electrochemistry of Metalloporphyrins in Nonaqueous Media. In: *The Porphyrin Handbook* / Eds Kadish K. M., Smith K. M. Guillard R. Academic Press, 2000. V. 8. Chapter 55. P. 1-114.