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Electroactive Polymeric Material with Condensed Structure on the Basis of Magnesium(II) Polyporphine

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Abstract

Previous publication of the authors presented evidences that electrochemical oxidation of Mg(II) porphine (fully unsubstituted porphyrin, MgP) in acetonitrile (AN) at a very low potential leads to deposition of films at electrode surface corresponding to typical electroactive polymers, with their reversible transition between the electron-conducting and insulating states depending on the electrode potential/oxidation level ("film of type I"). It is demonstrated in the actual publication that these films in contact with a monomer-free solution are subject to an irreversible transformation to quite a different material ("film of type II") under the influence of a higher positive potential (above 0.5-0.6 V *vs*. Ag/Ag^+ in AN). Films with the same properties may also be obtained directly by electrooxidation of the monomer, MgP, at a sufficiently high potential. Films of type II possess a high redox activity and electronic conductivity within the whole potential interval of above 3 V in the width. Their grayish color is related to a constant absorption intensity within the whole range of wavelengths studied (320-1000 nm). On the basis of a combination of experimental observations (ATR IR ad XPS) and literature data the molecular structure of this new material is assumed to be polymer chains of directly linked porphine units (with a partial loss of Mg cations), probably with multiple bonds (*meso-meso* and *β-β* type) between the neighboring units.

Keywords

electroactive materials · electropolymerization · magnesium porphine · unsubstituted porphyrin · conducting polymer · C-C coupling

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1. Introduction

Porphyrin-based systems are intensively studied during the last decades in view of their prospective physical and chemical properties [1]. In particular, numerous publications have been devoted to electroactive polymeric materials containing porphyrin fragments. The simplest approach is based on incorporation of porphyrin moieties with charged ionogenic groups into the growing conducting polymer film or powder owing to electrostatic attraction to the polymer matrix [2,3]. Another route is to link a porphyrin fragment to a polymerizable monomer (pyrrole, thiophene, aniline, etc.) via a saturated or conjugated bridge so that the polymerization of the monomer leads to attachment of porphyrin cycles to the polymer matrix by covalent forces [2,4]. In both cases these cycles are not included into the principal polymer chains. On the contrary, they are incorporated into principal chains in so-called "shish-kebab" coordination polymers where metalloporphyrins are connected by axial ligands of the metal cations [5].

More recently, *copolymers* or *co-oligomers* with alternating porphyrin and aryl, thiophene, aniline or ethynyl units inside the principal conjugated chain have been synthesized electrochemically [6-8] or chemically [9-12].

Linear or branched oligoporphyrin chains with a direct linkage between neighboring units in *meso* or/and β positions (with blocking substituents in other *meso*-positions of porphyrin rings) have also been synthesized [13-18].

Our study has been dealing with polymeric materials obtained by oxidation of the Mg(II) *porphine*, **MgP**, i.e. fully unsubstituted porphyrin (Fig. 1a). The previous publication [19] demonstrated that its potentiostatic or potentiodynamic oxidation in acetonitrile (**AN**) solution at a very low potential (within the first oxidation wave of the monomer) leads to deposition of an electroactive film (called "type I" below) composed from linear chains of MgP units ("polyporphine chains") linked in their *meso*-positions (Fig. 1b). This material possesses two electroactivity ranges of potential (where the matrix is charged positively or negatively and is electronically conducting) separated by a potential interval without a pronounced electroactivity or significant electronic conductivity.

The response of the deposited film in contact with background electrolyte solution is stable in the course of a multi-cycle treatment if the anodic limit does not exceed the potential of the first oxidation wave of MgP. On the contrary, for higher positive potentials this material is subject to an irreversible transformation giving rise to quite a different material ("type II"). Its properties are described in this publication.

2. Experimental

Electrochemical measurements (deposition of films and their study in monomer-free solution) were performed in AN under Ar atmosphere in three-electrode glass cell, with working electrode (WE) being Pt or glassy carbon (**GC**) disk or ITO-layer covered glass plate (with surface areas of about 0.01, 0.085 or 0.70 cm^2, respectively), with Pt wire as counter electrode and Ag/0.01 M $AgNO_3$ + 0.1 M $TBAPF_6$ + AN as reference electrode (RE) separated by double frit with intermediate background solution (0.1 M $TBAPF_6$ + AN).

All potentials in the paper are given *vs.* this RE. Its potential *vs.* aq. SCE is 0.32 V [20]. Formal potential of the Fc/Fc^+ couple in AN *vs.* RE is 0.10 V. More detailed information on the cell, electrode and procedures is available in reference [20]. Polymerization bath (with the same electrolyte, 0.1 M $TBAPF_6$) contained monomer solution, 0.25-1.0 mM MgP in AN. All potentiodynamic experiments (polymerization, redox response of films) were performed at the scan rate of 100 mV/s.

Homogeneity of the deposited film at the macroscopic scale was controlled by optical microscope (Nikon SMZ1000). After the deposition film was rinsed several times in AN, then transferred into background electrolyte solution in electrochemical or spectroscopic cell.

UV-visible spectra of solutions or film-coated ITO electrodes were recorded with VARIAN UV-visible spectrophotometer Cary 50 scan. IR ATR and XPS spectra of the polymer material were measured for films deposited on the surface of a Pt plate. For the sake of comparison such spectra were also recorded for monomer layers prepared by evaporation of several drops of MgP solution in acetonitrile placed on the Pt foil surface. Experimental IR transmittance spectra have been transformed into absorption ones, with subtraction of the background signal. Other experimental details have been given in previous publication [19].

3. Results and Discussion

3.1. Film deposition and transformation. Redox activity

As it has been described in [19], the potential cycling in the range not exceeding 0.5-0.6 V (curves 1 in Fig. 2) results in formation of an electroactive polymer film "type I", with its characteristic potential intervals of electroactivity and non-electroactivity (curve 1 in Fig. 3). This redox response is stable if the imposed potential does not exceed 0.4 V (short-time passage up to 0.5-0.6 V does not modify film properties, either).

If the film type I in contact with background electrolyte solution is subject to a more positive potential its redox response changes progressively, the transformation rate depending on the imposed potential (slow for 0.5-0.6 V, rapid for 1.0 V and higher). Series of curves 2-4 in Fig. 3 illustrates this evolution in the course of multi-cycle voltammetry with increasing the anodic limit of potential scans. In each cycle the anodic charge in this potential interval exceeds significantly the cathodic one which implies the further electrooxidation of the previously deposited film of type I into a new one of type II.

Fig. 4 presents another example of such transformation from type I to type II. The initial film was deposited potentiostatically at a low potential, 0.35 V (curve b in Fig. 4a) and its CV response in the potential range limited to 0.5

V is stable and corresponds to type I (series of curves 1 in Fig. 4b). Its further treatment with multi-cycle CV procedure with the fixed anodic limit of 1.3 V (series of curves 2 in Fig. 4b) reveals a very high anodic current and a great disbalance between the anodic and cathodic charges during the very first scan while the anodic branch in the range above 0.5 V approaches rapidly to a stabilized level during the further cycles at a much lower level. Also similar to the observation in Fig. 3, this transformation of the film results in a strong increase of both the anodic and the cathodic currents below 0.3 V including the whole "insulating range" of the initial film (curves 1).

Even though the shape of the i-E response is analogous with that for the electrical double layer the amplitude of the former is several orders of magnitude higher than that of the latter, as one can see from the comparison of the currents for the type I and type II in the potential range in Fig 3 where type I is insulating (-0.8 V, - 0.3 V). The attribution of the current for the type II to *redox* response of the film is also supported by its proportionality to the deposition charge, i.e. to the volume of the polymer layer. Further evidences of the redox activity of the film and its related electronic conductivity are presented below.

As a conclusion, the above transformation of the film changes radically its redox response within the whole potential range: the non-electroactivity interval disappears, and the intensity of the (anodic and cathodic) redox current approaches progressively to almost a constant value within the whole potential range, its width exceeding 3 V. Finally, this redox response becomes stable in the course of multi-cycle experiment.

The overall redox charge increases strongly compared to that for type I before transformation, due to both a broader potential interval and a higher current in the former non-electroactivity range. The redox charges for cathodic and anodic scans are well balanced after the end of the transformation.

Comparison of voltammograms for a film before (type I) and after (type II) transformation in Inset in Fig. 3 demonstrates its *irreversible* character, i.e. the modified response is observed even if the potential scan is limited (after the end of the transformation) to 0.4 V.

Another synthetic route consists in deposition of the film from the monomer solution at a higher positive potential, potentiodynamically (series of curves 2 in Fig 2) or potentiostatically (curve d in Fig 4a). The redox response of this potentiostatically deposited film in background solution is shown in Fig. 4d for potential scans limited to 0.5 V (curves 1). Its rectangular shape demonstrates that the film deposited at a high positive potential corresponds already to type II. Extension of the potential scans for this film to 1.3 V (curves 2) leads to the same rectangular shape of the redox response, without a strong electrooxidation current, thus confirming the attribution of the film to type II.

The film deposition at an intermediate potential (curve c in Fig. 4a) leads to the material with properties intermediate between types I and II (curves 1 in Fig 4c) which may then be transformed into pure type II by imposition of a higher positive potential (curves 2 in Fig. 4c).

3.2. Redox reaction at film surface. Conductivity

Faradaic reactions of solute redox species at the surface of the electrode coated with a film are frequently used for qualitative characterization of its electronic conductivity in the vicinity of the formal potential of the solute redox couple. As earlier for our films of type I [19] two moieties were considered, ferrocene (**Fc**) and titanocene dichloride (**$TcCl_2$**).

Oxidation of the former species takes place near the formal potential of the Fc/Fc^+ couple in AN (0.10 V [20]) for both films, type I (curve 2 in Fig. 5) and type II (curve 4 in Fig. 5). It implies that the conductivity near this potential is sufficient to transport the electronic charge between the electrode and polymer/solution interface where the heterogeneous electron transfer takes place.

Reduction of $TcCl_2$ gives quite different results for films of types I (curve 3) and II (curve 4). In the former case the reduction peak (about – 1.35 V) is shifted strongly compared to that for this reaction at the bare electrode, about – 1.00 V [20], which means that this film is electronically insulating in this potential range [19]. On the contrary, this faradaic process at the film of type II takes place near the potential at the bare Pt electrode, testifying in favor of the sufficient conductivity in this potential interval.

All these results match perfectly to the general principle of the correlation between the high levels of the redox activity of the film and of its electronic conductivity (in the “electroactivity potential ranges”), or their low values (in the “non-electroactivity range”, i.e. “insulating interval of potential”). In particular, this principle predicts that films of type II should function well as modified electrode for *any* potential (within the range of their stability).

As another feature of curves 2 and 3 in Fig. 5 is a low-intensity anodic peak observed near – 0.1 V. For the film in contact with Fc solution (curve 2) it represents expectedly an example of "prepeaks" which have been observed for numerous systems possessing *two* electroactivity ranges separated by a sufficiently broad "insulating potential range", see e.g. [21-24]. The electroactivity range may be related either to charging/discharging of the polymer matrix or to the redox transition of attached functional groups/complexes. The prepeaks originate from the "trapped charge" which is liberated when the system becomes again conducting after passage the insulating interval. The intensity of the same peak is much higher in the presence of solute $TcCl_2$ species. The reduction of them at the surface of the film type I on the onset of the n-doping potential range of the polymer leads to formation of solute products of this reaction in acetonitrile [20] which cannot be re-oxidized in the negative potential range because of the shift of this anodic wave at the bare electrode to – 0.6 V [20] where the polymer is already in the insulating state. As a result, the solute products are left in solution, diffusing from the film surface during the scan within the insulating range, while their remaining strengthens the prepeak due to the trapped charge of the polymer.

One should keep in mind that the whole above procedure is based on the assumption which is usually not discussed at all: the film must cover the electrode surface completely, without non-coated areas or/and holes/pores in it reaching the surface of the substrate. The validity of this assumption for films of type I follows from the above shift of the wave for $TcCl_2$, without any wave near –1.0 V.

This argumentation does not work for films of type II since the waves for both reactants overlap with the corresponding waves for bare Pt. Analysis with optical microscope did not reveal visible damages of the film continuity after its transformation into type II but the appearance of microdefects cannot be completely refuted.

In this context the direct evaluation of the electronic conductivity of the film of type II is of great importance. We used the same method to measure the sum of the electrolyte solution, R_{sol}, and the high-frequency resistance of the film, R_{film}, from the short-time behavior of the chronoamperometric curves [19]. Fig. 6 reveals a drastic difference of this characteristic between films of types I (points 1) and II (points 2). For type I; it increases strongly within the interval of the film non-electroactivity (- 1.6V, - 0.2 V), due to its electronically insulating behavior for these potentials [19]. On the contrary, for a film of type II the measured value is close to the solution resistance (line 3 in Fig. 6) within the whole range of potentials, i.e. the electronic resistance of this film is much less than 10 Ω for all potentials.

These data for both films agree perfectly with the above principle, in particular, demonstrating that films of type II are both redox active and electronically conducting within the whole potential range of their stability (above 3 V in width).

3.3. UV-visible spectroscopy

Optical microscopy shows a grayish color of films type II and a relatively uniform macrostructure. The number of macrodefects depends on the deposition conditions, film thickness, cell configuration, etc., i.e. they are not inherently related to the microstructure of the film.

Fig. 7 shows a drastic change of the UV-visible spectrum of the film type II (curve 3) compared to those of the solute monomer (curve 1) or film type I (curve 2). Both Soret and Q-bands disappeared completely for type II (a very weak band is left near the position of the Soret band for the monomer) so that the intensity of absorbance became almost constant within the whole interval of wavelengths under study (from 350 nm to 1000 nm), in conformity with the gray color of the film.

3.4. XPS spectra

Spectra of C, N and Mg for the film of type II (curves 3 in Figs. 8a,b,c) were analyzed, in comparison with those for the monomer, MgP (curves 1), and film of type I (curves 2) [19]. Shapes of bands for Mg 2s (Fig. 8a, maximum at 1303.2 eV) and C 1s (Fig. 8b, maximum at 284.5 eV) are practically identical for all these three systems. The carbon spectrum shows bands corresponding to the C-C and C-N bonds in these materials [19], while no oxygen containing peaks were found, i.e. no bonds of C or N with oxygen are formed, in the course of in situ treatments under Ar or the film transfer to XPS device via air.

N 1s spectra for all three systems (Fig. 8c) are composed from the principal peak at 307.7 eV and a shoulder shifted to higher energies by about 1.9 eV. However, while the relative weights of these two bands are about 80% : 20%. for the monomer (curve 1) and film type I (curve 2), this ratio changes to about 65% : 35% for film of type II (curve 3), without peaks for oxygen-containing bonds. This structure for the former systems corresponds perfectly to literature data for pure Mg(II) porphyrin, MgTPP [25]. The spectrum for type II is intermediate between those for pure Mg(II) porphine/porphyrin and for *metal-free* porphine/porphyrin, in which both components in the N 1s spectrum should roughly be of equal intensities, i.e. about 50% : 50% [26,27]. Thus, the observed spectrum for type II implies a significant loss of Mg cations from the film.

The latter explanation has been confirmed by the analysis of the ratio of the intensities for Mg and N peaks [19] which shows a marked loss of Mg(II) cations, from 10% to 40%, for type II, while no significant loss was found for type I.

3.5. IR spectra

Fig. 9 compares IR data for two porphines, with Mg(II) (MgP) (a) or free-base one (H_2P) (b), and for films of type I (c) and II (d). While the absorption spectra for MgP and type I are surprisingly similar so that there are no doubts that this polymer is composed from entire MgP units [19] the spectrum for type II looks quite different, with several broad bands instead of previous sets of low-intensity peaks. However, the further analysis shows that all three principal bands of MgP and type I, about 990, 850 and 1060 cm^{-1}, are still present after transformation to type II, with their marked broadening, though.

Another interesting feature of the latter spectrum (Fig. 9d) is a peak (of a weak intensity) at about 690 cm^{-1} which is absent in Figs 9a,c but visible in the spectrum of H_2P and which corresponds to out-plane N-H vibrations. This observation correlates well with the partial demetallation of the polymer in the course of its transformation from type I to type II (on the basis of XPS data).

3.6. Other characterization methods

Powder XRD spectra for the film of type II at Pt plate surface only show peaks of the substrate, similar to those for type I. It implies the absence of any crystalline structure.

Analogously to the treatment of the film type I, we tried to dissolve the film of type II or at least to extract its components by THF. However, UV-visible spectrum of the THF phase does not reveal any extracted substances, unlike the case of type I.

3.7. Electronic and molecular structure

The above data for the redox activity and the electronic conductivity as functions of the potential as well as for the UV-visible-NIR absorbance *vs.* wavelength reveal a crucial difference in the electronic properties of types I and II. Since the former demonstrates a qualitative resemblance with conventional "conjugated polymers" (e.g. polythiophene or polyparaphenylene) its electronic level structure in the neutral state should correspond to a semiconductor with conduction and valence bands while the polymer charging results in creation of new delocalized electronic states inside the forbidden zone, responsible for the increased electronic conductivity [19]. On the contrary, all data for type II implicate quite a different energy band structure resembling an electronic conductor in which the mobile charge carriers are not coupled with molecular vibrations, like in metals or in conducting carbon materials, while the Fermi level is located inside a broad energy band ("metallic energy structure") for all degrees of the film charging attained by its oxidation or reduction from the neutral state.

This variation of the electronic properties from type I to type II has to originate from the change of the molecular structure. Even though one cannot exclude completely the possibility of the porphine decomposition in the course of this transformation there are various indirect data testifying in favor of the conclusion that this unit is still retained inside type II:

- XPS spectra of all elements are very similar for types I and II, except for the more intensive shoulder in the N 1s spectrum, this specific feature obviously originating from the partial loss of Mg cations;
- No appearance of C-O or N-O bonds has been registered in XPS spectra;
- All three principal vibration bands of the monomer, MgP, and polymer type I are still visible for type II, despite their broadening.

Within the framework of this hypothesis one can discuss possible molecular structures. Since type II may be obtained by oxidation of type I, without C-O bond formation, the polymer chains composed by porphine units (partially demetallated) with *meso-meso* bonds between them should retain inside the new structure. New chemical bonds might be formed either/both between the same neighboring (already linked) units or/and between units of the neighboring polymer chains (Figs 10a,b,c), thus giving a *condensed* polymeric structure.

In both variants the ability of neighboring porphine units to rotate around the molecular bond(s) between them practically disappears. As a result, electronic states at such lattice are not coupled with molecular rotations (which are expected to be responsible for the insulating character of the neutral state in type I [19]), a prerequisite for the electronic energy structure leading to observed redox, conductive and optical properties of this system. This configuration should expectedly retain its planar character for any degree of its oxidation or reduction, which is in conformity with observed redox and spectral properties of this system.

According to ref [28], treatment of oligomeric chains with *meso-meso* bonds between neighboring Zn(II)-porphyrin units (analog of our type I polymer) by a strong chemical oxidizer leads to formation of *condensed tapes*, i.e. linear one-dimensional oligomeric structures with *three* (*meso-meso* and two *β-β*) bonds between each couple of neighbors. Since our transformation between the types I and II also occurs under the action of a stronger oxidizer (a higher positive potential) compared to that used for the synthesis of the material of type I, it gives an evidence in favor of a similar structure (Fig. 10a) for films of type II. One may note that the *solid-state* transformation between the molecular structures in Figs. 1b and 10a takes place *within a single molecule*. On the contrary the formation of two-dimensional structures (like those in Figs 10b,c) requires a *perfect adjustment of neighboring polymer chains* which is hardly available in the irregular starting polymeric material (Fig. 1b).

This conclusion is also supported by the correspondence between properties of such “fused tape *finite-length* oligomers” [28], for which the HOMO-LUMO separation is decreasing with increase of the chain length, tending to zero for sufficiently extended chain lengths, and our material of type II having apparently no gap between occupied and unoccupied electronic levels, according to the redox and optical data.

Moreover, calculation of electronic levels of a fused Zn porphine *chain* (analogous to that in Fig. 10a) as a function of the chain length [29] predicts a progressive diminution of the HOMO-LUMO gap, with metallic behavior for a long “tape”, while a semiconductor limit is expected for the similar 2D “sheet” (analog of Fig. 10c). The former prediction corresponds perfectly to redox and optical properties observed for our type II films, thus giving an additional argument in favor of the structure shown in Fig. 10a.

Interestingly, a qualitatively similar shape of the redox response of electrochemically deposited polymer films has recently been observed for phenyl- or thiophene-functionalized porphyrins [6] whose molecular structure was described as a linear or two-dimensional *copolymer* with alternating porphyrin and aryl/thiophene units. The absence of any substituent in our monomer, MgP, in combination with other data for this system (in particular, the generation of film of type II from that of type I whose molecular structure is reliably determined [19]) ensures that the film is formed by direct links between these monomer units, without any intermediate groups.

4. Conclusions

Results of our studies exposed in [19] and this paper show that electrochemical oxidation of magnesium(II) porphine, MgP, results in deposition of electroactive polymer films at the electrode surface, their properties being crucially dependent on the polymerization potential (films of types I and II).

The former material (type I) resembles closely conventional conjugated polymers (CPs), with their complete change of the electronic energy level structure as a function of the oxidation level, related expectedly to transition between a planar molecular organization for the electronically conducting states and the structure with twisted orientations of neighboring monomer units for the insulating state. However, unlike conventional CPs the type I film does not show a drastic negative shift of the oxidation potential, compared to its monomer, expectedly due to a large size of the monomer building block [19]. Another specific feature is a relatively low potential of its chemical transformation, compared to the "overoxidation" phenomenon for conventional CPs.

The oxidation at a more positive potential, or holding of the film of type I within such a higher potential range, results in quite a different material (type II) which is redox active and electronically conducting within the whole broad potential interval, without any “insulating gap”. This irreversible transformation between the types I and II is accompanied by the change of the other properties, in particular of absorption in the UV-visible-NIR and IR regions.

The molecular structure of type I is assumed to be a linear chain of *meso-meso* bonded monomer units, MgP (Fig 1b), with rotation along these bonds in the course of transitions between “conducting” and “insulating” states. The oxidation at a higher potential (type II) leads presumably to formation of additional intra- or/and intermolecular C-C bonds. As a preliminary hypothesis these may be two extra *beta-beta* bonds between the neighboring units in the polymer chain (already existing in type I before the transformation), giving rise to “fused tapes” (Fig. 10a) which keeps the whole molecule in a planar configuration, independent of its oxidation level, in conformity with specific redox and optical properties of this material. A partial loss of Mg cations during this process due to increase of the local acidity (related to the new C-C bond formation) represents probably a side process which is not responsible for the difference between the types I and II.

One can expect that these new materials with interesting properties and their derivatives will find applications in energy sources, catalysis, molecular electronics, nonlinear optics, photovoltaics, etc.

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Figures and Legends

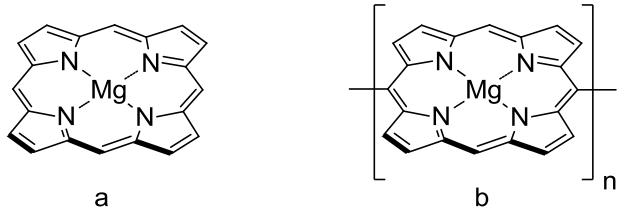

Fig. 1 Schematic structures of the monomer, MgP (a) and of the polymer, pMgP, of type I (b)

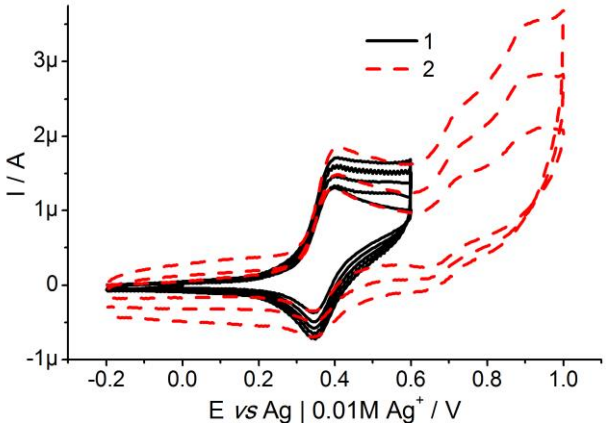

Fig. 2 CV response of bare Pt electrode in contact with monomer solution (0.5 mM MgP + 0.1 M $TBAPF_6$ in AN) during multi-cycle experiment with anodic limit: 0.6 V (curves 1) or 1.0 V (curves 2, not all intermediate scans are shown for the sake of visibility)

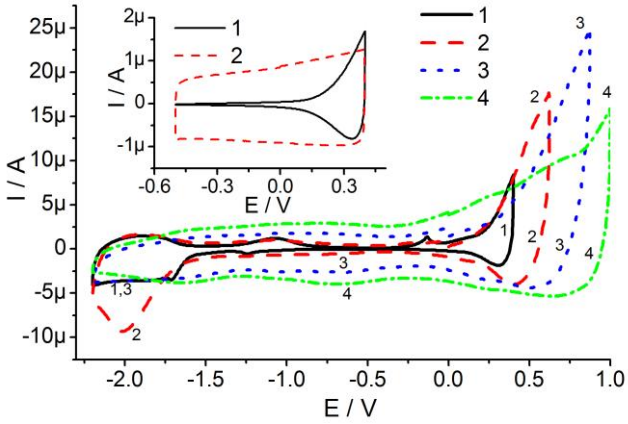

Fig. 3 Progressive transformation of film type I (curve 1) in the course of multi-cycle treatment with variable anodic limit (curves 2-4, not all intermediate scans are shown for the sake of visibility) into film type II (curve 4). Inset: CV responses of films type I (curve 1) and type II (curve 2) in the interval: - 0.5 V, 0.4 V

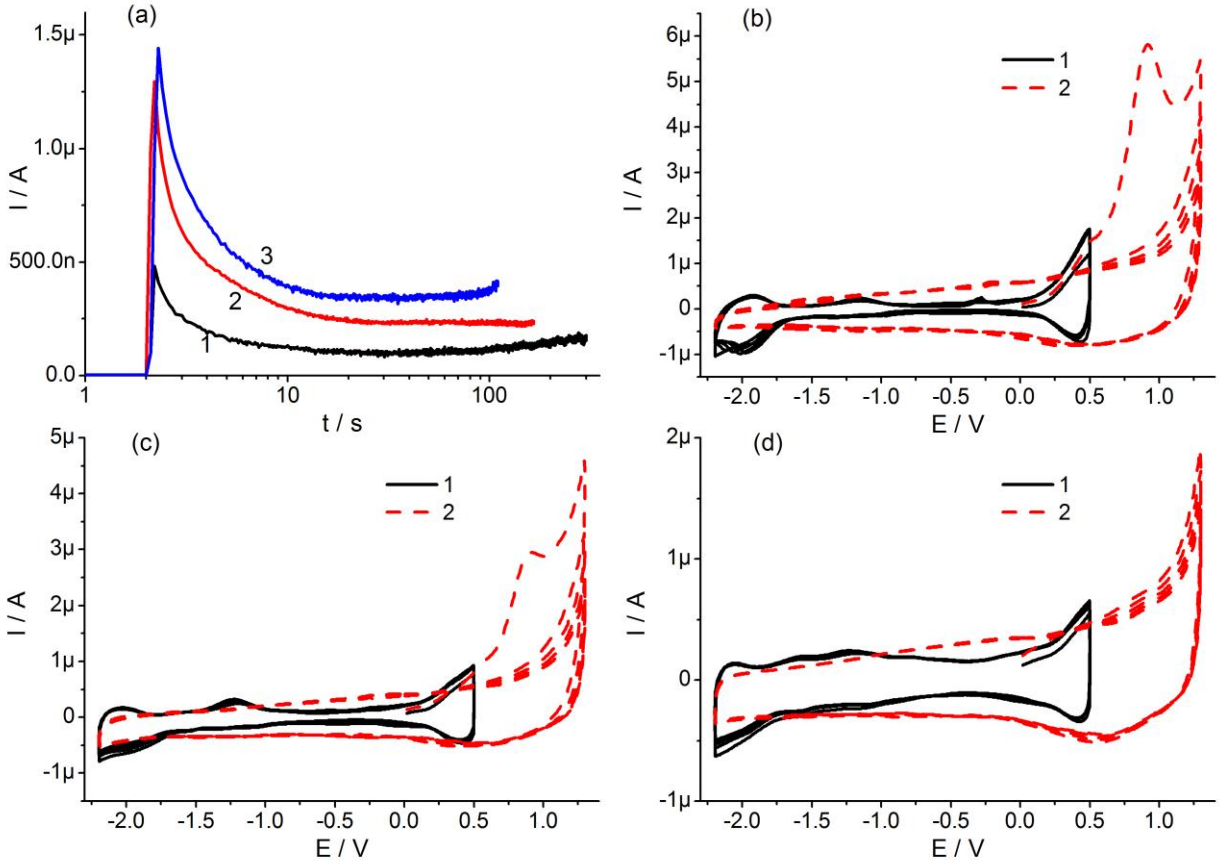

Fig. 4 (a) Deposition curves for various deposition potentials, E_{dep}: 0.35 V (b), 0.5 V (c), 0.7 V (d). For all curves: monomer concentration, 0.25 mM MgP, deposition charge, 40 µC. Figs. 4b, 4c and 4d present CV responses of these three films deposited at various potentials (curves b, c or d in Fig 4a, correspondingly) in background electrolyte with the anodic potential limit equal to 0.5 V (series of curves 1, stable response) or to 1.3 V (series of curves 2)

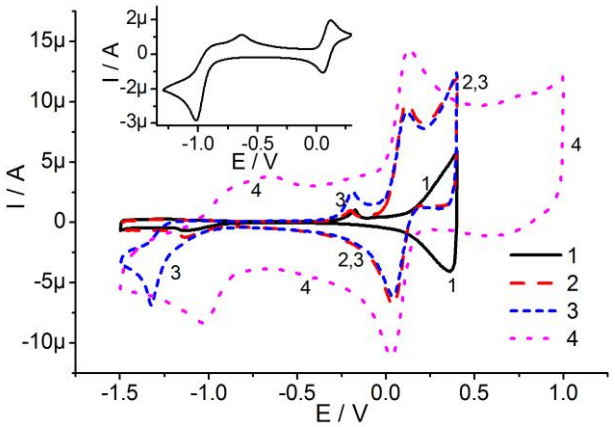

Fig. 5 Stabilized CV responses of film deposited at 0.35 V from 0.5 mM MgP + 0.1 M $TBAPF_6$ in AN with deposition charge, 377 µC. (1) Deposited film type I in monomer-free solution; (2) The same after addition of 2 mM Fc; (3) The same after addition of 2 mM $TcCl_2$; (4) The same film after its transformation into type II in contact with the mixed Fc + $TcCl_2$ solution. 100 mV/s. Inset: Bare electrode in the mixed Fc + $TcCl_2$ solution.

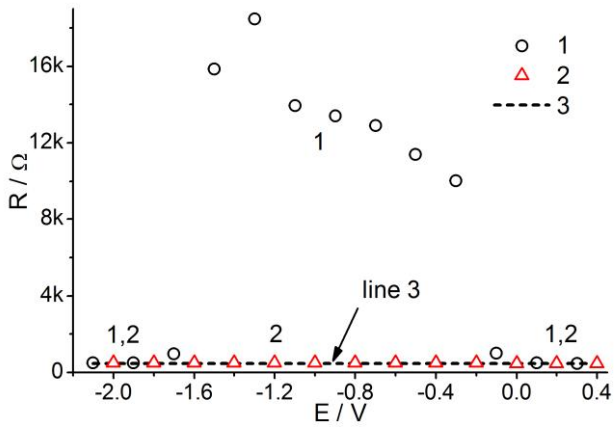

Fig. 6 Dependence of the total resistance, $R_s + R_f$ on the electrode potential. Pt disc electrode coated with deposited film whose thickness, about 300-450 nm, was estimated with the use of Eqs (2), (6') [19] for the total deposition charge of 30 mC/cm^2. (1) film type I, (2) after oxidative transformation to type II, (3) high frequency resistance of the cell without film.

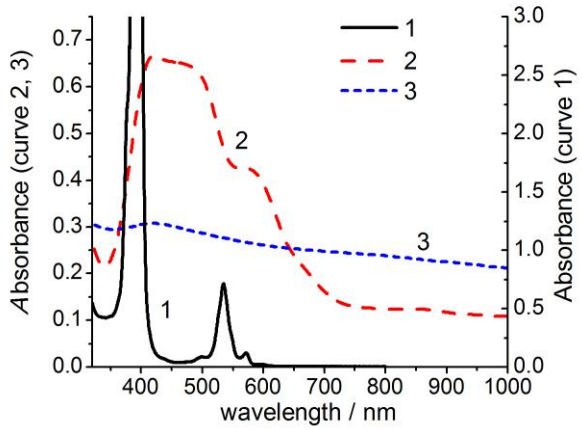

Fig. 7 UV-visible spectra: (1) monomer in AN solution, (2) film type I (deposited at 0.35V on ITO surface), (3) the same film after its oxidative transformation into type II.

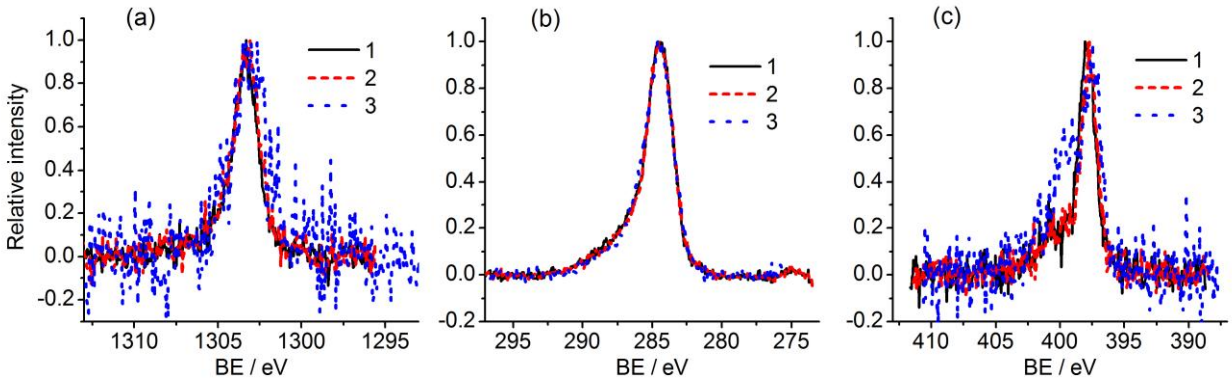

Fig. 8. Normalized XPS spectra for monomer, MgP (line 1), and for films of type I (line 2) and II (line 3): (a) Mg 2s, (b) C 1s, (c) N 1s.

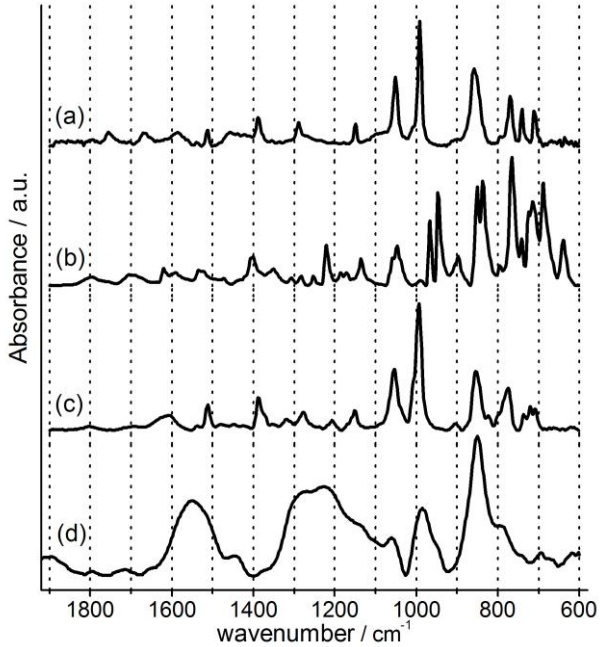

Fig. 9 Experimental ATR IR spectra (after baseline correction): (a) MgP monomer (layer on Pt plate), (b) H_2P powder, (c) film type I, (d) film type II.

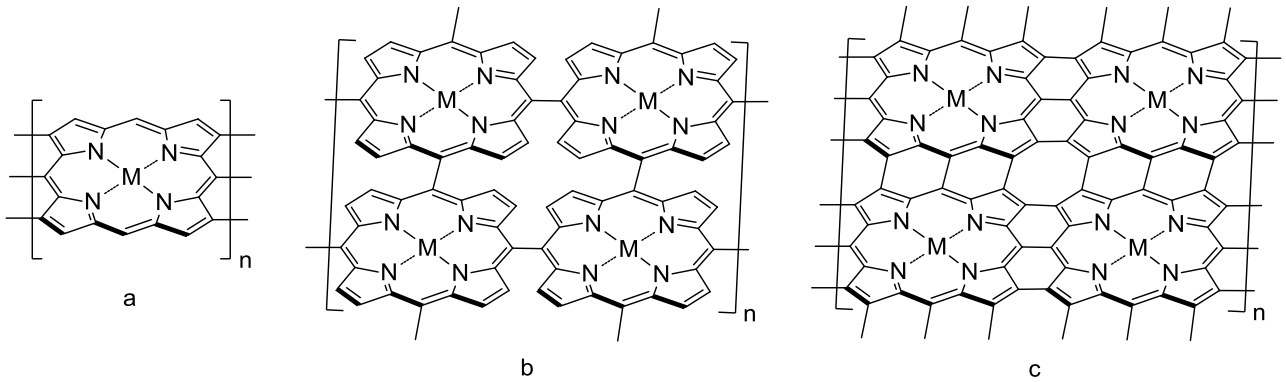

Fig. 10 Schematic molecular structures assumed for the material of type II: (a) “Fused tape” with triple (meso-meso and two β-β) bonds between neighboring units; (b) Two-dimensional (2D) structure with single meso-meso bonds between porphine units; (c) “Fused sheet” with triple (*meso-meso* and two *β-β*) bonds between neighboring units. Symbol "M" in these structures corresponds to various porphine building blocks which coordinate either magnesium cation (as in MgP), or two hydrogen atoms (as in its free-base form, H_2P), because of a partial demetallation of this material in the course of transformation from type I to type II.