Synthesis, Electronic Structure and Study of Ytterbum Tetraphenylporphyrin Complexes Stability by Photoelectron Spectroscopy and Thermogravimetry*

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Metalloorganic complexes of rare earth elements with porphyrins have attracted attention over the past years in view of potential applications as templates for biology, nanotechnology and medicine. For deeper understanding and studying of their properties the knowledge of electronic structure and bonding in these compounds is required and should be investigated essentially by a photoelectron spectroscopy.

In present work the electronic structure and stability of tetrakis-porphyrins and its ytterbium complexes were studied experimentally by X-ray (XPS) photoemission spectroscopy. The X-ray photoemission data show the different atomic constituents in accordance with its states in molecules which can be related to the peaks of N1s, C1s, O1s, Yb4d appearing in the electronic spectra. In the tetraphenylporphyrin free base spectrum of the N1s state core levels there are two peaks of N1s which were assigned to sp^3 and sp^2 nitrogen respectively (pyrrol- and aza-states). In Yb metalloporphyrin charge distribution is more uniform for N1s spectra and thus wide single peak of N1s states reflects small difference between pyrol- and aza-nitrogen. The analysis of Yb4d electronic states shows that spectra do not consist of the spin-orbit split doublet, but instead is composed of asymmetric peak with multiplet splitting. Divalent Yb has a filled 4f shell, i.e. a $4f^{14}$ configuration, and the 4d spectra shows the doublet with 3:2 ratio, while for trivalent Yb, $4f^{13}$, the 4d peaks consist of a multiplet. The spectrum analysis demonstrated the multiplet splitting of Yb 4d and trivalent state in Yb(acac)-5,10,15,20-tetrakis-porphyrins.

The research of thermal stability of tetraphenylporphyrin, octabrominetetraphenylporphyrin, ytterbium acetylacetonate octabrominetetraphenylporphyrin by X-ray photoelectron spectroscopy and thermogravimetry measurements in the range of temperatures of 30–450°C (when heating in ultrahigh vacuum) has shown destruction of the octabrominetetraphenylporphyrin and ytterbium acetylacetonate octabrominetetraphenylporphyrin after warming up higher than 150°C while free base porphyrines (tetraphenylporphyrines) have shown thermal stability under vacuum conditions.

Keywords: *tetraphenylporphyrin, ytterbium, octabrominetetraphenylporphyrin, thermogravimetric, photoelectron spectroscopy, thermal evaporation.*

Introduction

Metalloporphyrins can be used as an active medium for optical communication [1, 2], processing of optical and electric signals [3] and information storing [4] due to the nonlinear optical properties of these compounds. Porphyrins as low-dimensional conductors [5, 6] attract interest in the field of nanotechnology and creation of elements and devices based on separate

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macromolecules sensitive to the effect of electric, magnetic and electromagnetic fields [2–4]. In order to study profoundly the physical and chemical properties and the features of the electronic structure of the valent zone of macroheterocyclic compounds of the porphyrin series it is very promising to study metal complexes with rare earth elements.

Interest in porphyrin complexes with ytterbium shown by scientists of various specialties is caused by the fact that these substances have unique biological and physicochemical parameters, and also by the possibility of applying them in medical studies as active components of modern electronic and optoelectronic devices [7].

The design of new devices using metal complexes requires detailed knowledge of the electronic structure of these compounds and the development of technology for creating thin-film structures. The physicochemical stability of metal complexes and the possibility of implementing thin-film technologies are key aspects of the operability of devices using these compounds as an active medium.

This work is devoted to studying the electronic structure of ytterbium complexes of tetraphenylporphyrin and its octabromo derivative by X-ray photoelectron spectroscopy (XPS), studying the thermal stability of these compounds and the possibility of creating thin films by thermal spraying.

Experimental

1,2,4-Trichlorobenzene, 1,2-dichlorobenzene (Acros Organics), dimethyl formamide, chloroform, ethanol, methanol (Chimmed) and silica gel 60 (0.040–0.063 mm) (Merck, Germany) were used for the study. Ytterbium acetyl acetonate ($Yb(acac)_3$), tetraphenylporphyrin (TPP), octabromotetraphenylporphyrin ($TPPBr_8$) and ytterbium complexes of porphyrins (Yb(acac)TPP and $Yb(acac)TPPBr_8$) were synthesized according to the techniques described in [8]. Electronic absorption spectra were measured with the use of a Helios Alpha Local Control System "TermoSpectronic" spectrophotometer (USA) in chloroform. Mass spectra were recorded by means of an Ultraflex TOF/TOF spectrometer ("Bruker Daltonics", Germany) with the use of 2,5-dihydrobenzoic acid as a matrix.

Preparation of thin-film coatings

In order to obtain thin-film coatings based on porphyrins and their metal complexes we applied thermal evaporation and deposition on a substrate in high vacuum. Porphyrins spraying was carried out with the use of a universal vacuum post VUP-5 at a pressure in the camera of 4–$5\cdot10^{-6}$ torr. Porphyrin complexes were sprayed from an evaporator (quartz crucible) with resistive heating. Distance from the crucible to the substrate was 10 cm. Spraying rate was controlled according to indications of a quartz thickness gage. Heating was carried out until a constant sputtering rate was attained. Then the substrate was moved to the spraying area, and porphyrin spraying was carried out. At the end of exposure time the substrate was removed from the spraying area, and heating was switched off. The evaporator temperature was controlled with the use of a chromel-alumel thermocouple. The films structure was analyzed by XPS.

Study on the electronic structure of the porphyrin complexes with ytterbium was conducted at the Institute of Solid State Physics of the Russian Academy of Sciences with the use of a "KRATOS AXIS ULTRA DLD" photoelectron spectrometer with a spherical sector analyzer, with the possibility of heating a sample, with ionic guns and with ultra-violet and X-ray sources. Experiments were made in ultra-high vacuum ($5 \cdot 10^{-10}$–$3 \cdot 10^{-9}$ torr) with the use of monochromated radiation Al Kα 1486.6 eV (mono) (energy resolution 0.48 eV, binding energies were calibrated according to Ag $3d_{5/2}$ line).

Samples for studying the electronic structure were prepared by chemical deposition of a solution of a porphyrin metal complex in chloroform or tetrachloromethane on a silver substrate, and also by mechanical pressing in an indium substrate, which allowed minimizing the thickness of the applied sample and, respectively, the charging processes. Because the samples were prepared *ex situ*, they might contain impurities from the atmosphere (adsorption), such as water vapor, carbon dioxide and other gases. Therefore, before carrying out the XPS study the surface of the porphyrin and metalloporphyrin samples could be additionally purified by annealing (0.5–1 h) at 150°C *in situ* in the ultra-high vacuum of an electronic spectrometer (10^{-9} torr).

Thermogravimetric analysis (TGA) of the compounds was carried out by means of a Setaram Setsys EVO 16/18 device (Setaram, France). The device was equipped with a gas system with flow controllers allowing to conduct studies in the atmosphere of oxygen, air, argon, carbon dioxide and in vacuum. The maximum operating temperature during the study was 450°C, instrumental error at the range of weight change ± 20 mg was 10 μg.

Results and Discussion

Synthesis of porphyrin complexes with ytterbium

The target compounds were obtained according to the schemes submitted in Figures 1 and 2, refluxing a 5–10-fold surplus of ytterbium acetyl acetonate, the free bases of tetraphenylporphyrin or its octabromo derivatives in 1,2,4-trichlorobenzene in an inert atmosphere.

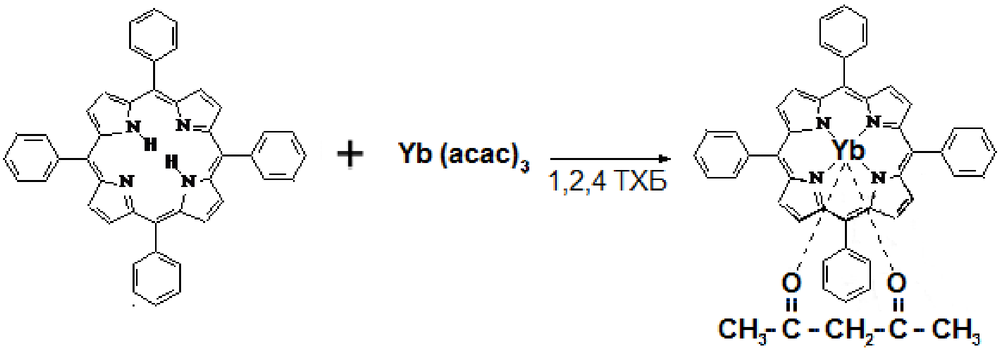

Figure 1. Scheme of synthesizing tetraphenylporphyrin ytterbium complex Yb(acac)TPP.

[TXБ means TCB]

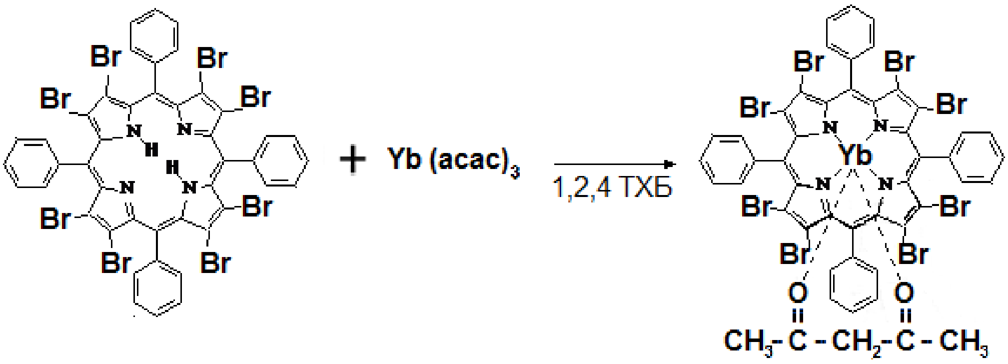

Figure 2.

Scheme of synthesizing octabromotetraphenylporphyrin ytterbium complex

Yb(acac)$TPPBr_8$.

[TXБ means TCB]

Specific features of electronic structure of complexes of porphyrins with ytterbium

The XPS spectra of the studied compounds contain peaks of deep (core) levels C1s, N1s, O1s, Yb4d, Br3d and Br3p. Impurities present on the surface of the metal complexes after cleaning (heating in vacuum to 100°C for 0.5–1.5 h) are slight except for silicon traces (Si2s peak at 150 eV and Si2p at 100 eV), which perhaps remained after the synthesis. The relative concentrations of the elements correspond at a first approximation to the chemical composition of the compounds.

Special attention was paid to studying the electronic structure of the precursor basic compounds (TPP and $TPPBr_8$) (Figure 3, 4), on the basis of which the ytterbium complexes of porphyrins were synthesized.

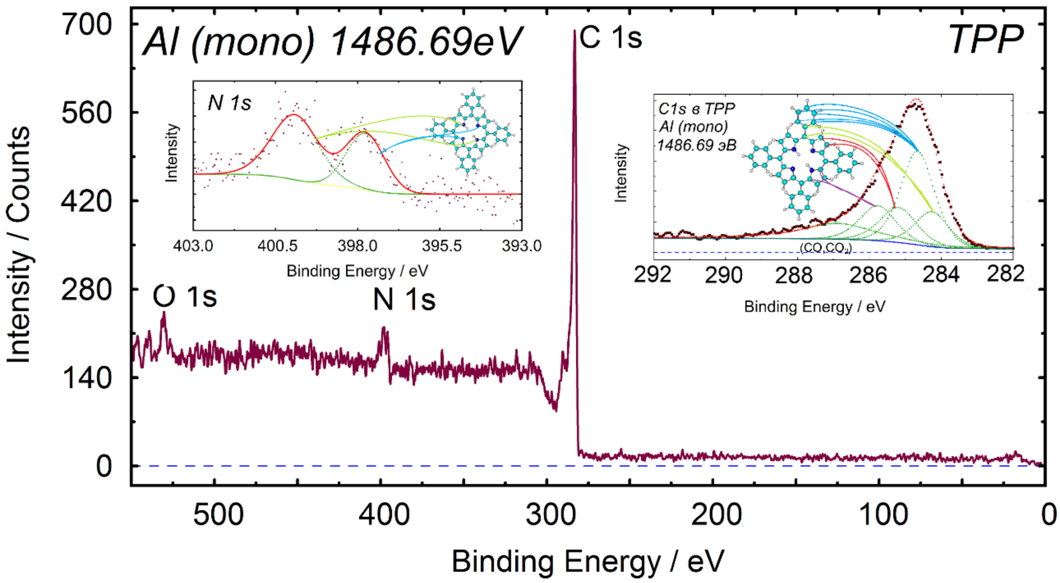

Figure 3. Survey XPS spectrum of tetraphenylporphyrin and high-resolution spectrum of N1s and C1s range.

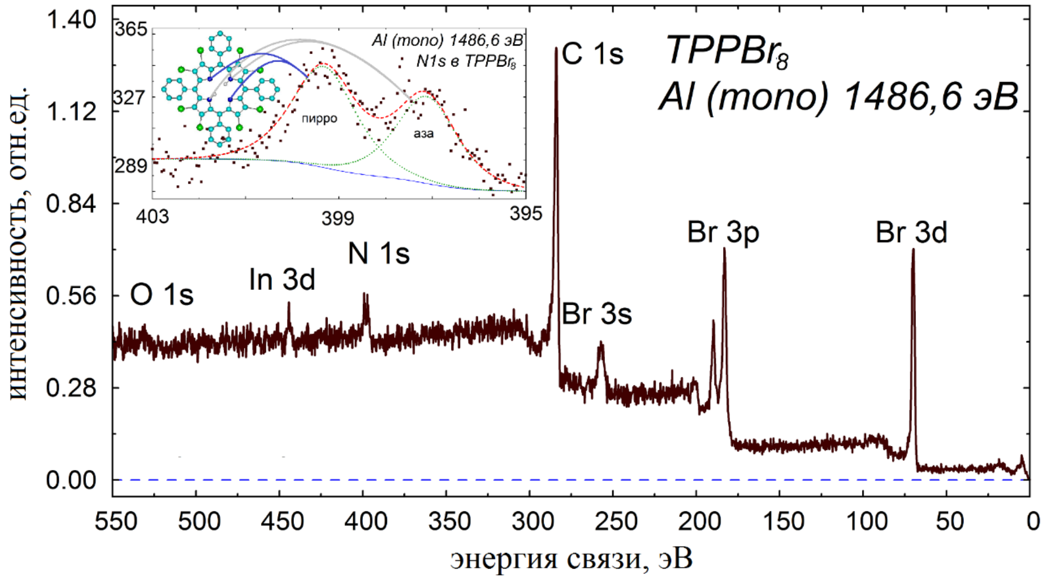

Figure 4. Survey XPS spectrum of octabromotetraphenylporphyrin and high-resolution spectrum of N1s range.

[интенсивность, отн. ед. means Intensity, rel. units; эВ means eV; энергия связи, эВ means Binding energy, eV]

The XPS spectra of the core N1s levels of tetraphenylporphyrin states (Figure 3) and $TPPBr_8$ (Figure 4) contain a distinct characteristic two-peak structure with binding energies of 399.4 and 397.2 eV in case of TPP, 399.3 and 397.1 eV in case of $TPPBr_8$ attributed to the nitrogen atom in the pyrrole ring (sp^3 bond configuration) and to the aza-group (sp^2), respectively. This is in good agreement with the results for thiolporphyrin [9] and related phthalocyanine compounds [10].

The XPS spectra of the core C1s level of the studied compounds contain a broad wide peak caused by photoemission of various states of carbon in nonequivalent positions in the molecule (aromatic, pyrro- and aza-). Analysis of the nonequivalent positions of carbon in the macrocycle is presented in Figure 3. Similar values of C1s states for various porphyrins were obtained previously by XPS also in case of related pyridylporphyrins [11]. The ratio of the quantity of atoms of equivalent carbon states to the total quantity of carbon atoms was close to the values of the relative area of the simulated peaks.

The survey photoelectron spectra of the studied ytterbium metal complexes contain peaks of all the elements (C, N, O, Yb and Br) entering into the composition of the compounds.

The XPS spectra of the studied metalloporphyrins (Figure 5) show one broad peak of N1s states (overlapping with the Yb4p peak). This indicates electron density levelling between pyrro- and aza-N, which is in good agreement with the data [9] obtained for metalloporphyrins (M = Fe, Co, Mn and Ni) and copper phthalocyanines [12, 13]. In order to take into account the contribution of the Yb4p$_{1/2}$ peak to the spectrum of the N1s level the splitting of the core Yb4p level in ytterbium(III) oxide was additionally considered.

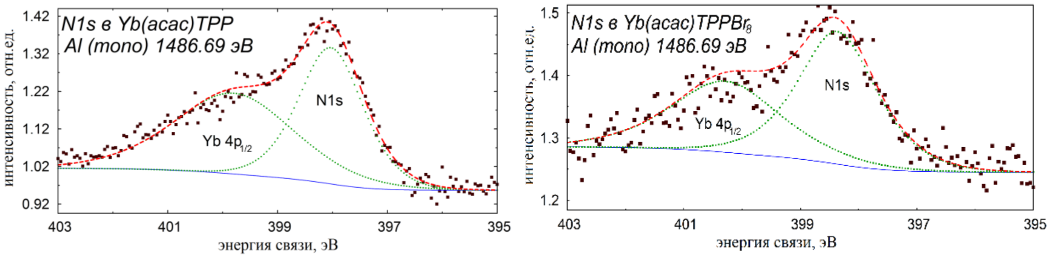

Figure 5. High-resolution spectrum of N1s peak:
left – in Yb(acac)TPP, right – in Yb(acac)TPPBr$_8$.
[интенсивность, отн. ед. means Intensity, rel. units; эВ means eV; в means in;
энергия связи, эВ means Binding energy, eV; мультиплет means multiplet]

Using the parameters of preliminary high-resolution spectrum of the core Yb4d level of ytterbium(III) oxide and metallic ytterbium (Figure 6) we obtained a high-resolution spectrum of Yb4d states for Yb(acac)TPP and Yb(acac)TPPBr$_8$. The high-resolution spectrum of the core Yb4d level of ytterbium metalloporphyrins shows a distinct multiplet, which indicates the trivalent state of ytterbium in the compounds.

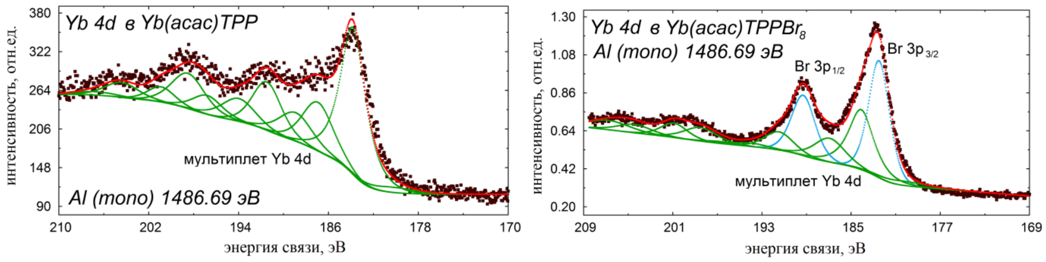

Figure 6. High-resolution spectrum of Yb4d peak:

left – in Yb(acac)TPP, right – in Yb(acac)TPPBr$_8$.

[интенсивность, отн. ед. means Intensity, rel. units; эВ means eV; в means in; энергия связи, эВ means Binding energy, eV; мультиплет means multiplet]

The spectrum of Yb4d levels of Yb(acac)TPPBr$_8$ (Figure 6) contains overlapping Yb4d and Br3p peaks. In order to obtain a correct high-resolution the spectrum of Br3p level in TPPBr$_8$ porphyrin was previously recorded. It has the shape of a doublet with areas ratio 1:2. Using the parameters of the high-resolution spectrum of Br3p level in TPPBr8 porphyrin, the Br3p doublet in Yb4d level spectrum of Yb(acac)TPPBr$_8$ was correctly described.

The XPS spectrum of Br3d level in TPPBr$_8$ (Figure 7) has a distinct doublet of Br3d$_{5/2}$ and Br3d$_{3/2}$ peaks. The ratio of the areas under its components is 3:2, which indicates a single state of bromine in the TPPBr$_8$ molecule.

The XPS spectrum of the core Br3d level of Yb(acac)TPPBr$_8$ (Figure 7) contains a spectrally non-resolvable broad peak that can be described as two doublets of Br3d$_{5/2}$ and Br3d$_{3/2}$ peaks with areas ratio 3:2. This indicates the existence of two states of bromine in the compound, which can give evidence of the presence of impurities formed in the course of the synthesis.

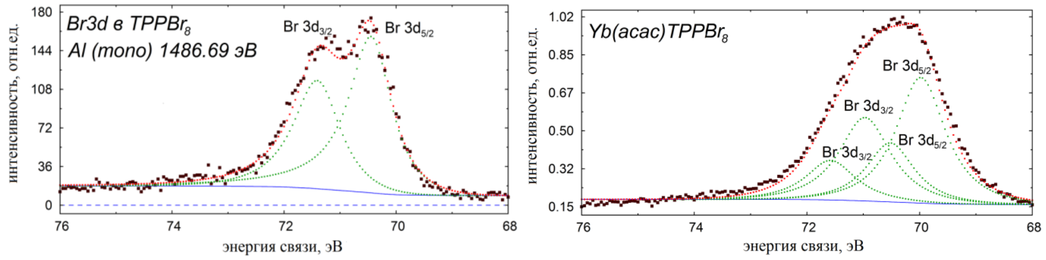

Figure 7. High-resolution spectrum of Br3d:

left – in TPPBr$_8$, right – in Yb(acac)TPPBr$_8$.

[интенсивность, отн. ед. means Intensity, rel. units; эВ means eV; в means in; энергия связи, эВ means Binding energy, eV; мультиплет means multiplet]

In the spectra of compounds containing oxygen, the O1s line corresponds to the oxygen atom in the acetylacetonate group bound to the macrocycle.

Stability of porphyrin complexes upon thermal impact in vacuum

Analysis of the elemental composition of the applied films by photoelectron spectroscopy showed that TPP and Yb(acac)TPP evaporate congruently. In the XPS spectrum of thermally deposited Yb(acac)TPP film peaks of all the elements comprising the compound are present, and specific features related to ytterbium tetraphenylporphyrins are observed, such as the one-peak structure of the N1s area, the broad carbon peak caused by several nonequivalent states of carbon in the compound and the multiplet splitting of the Yb4d line (Figure 8). In contrast, this method showed a change in the elemental composition of octabromo derivative, which indicates decomposition or incongruent evaporation of these compounds.

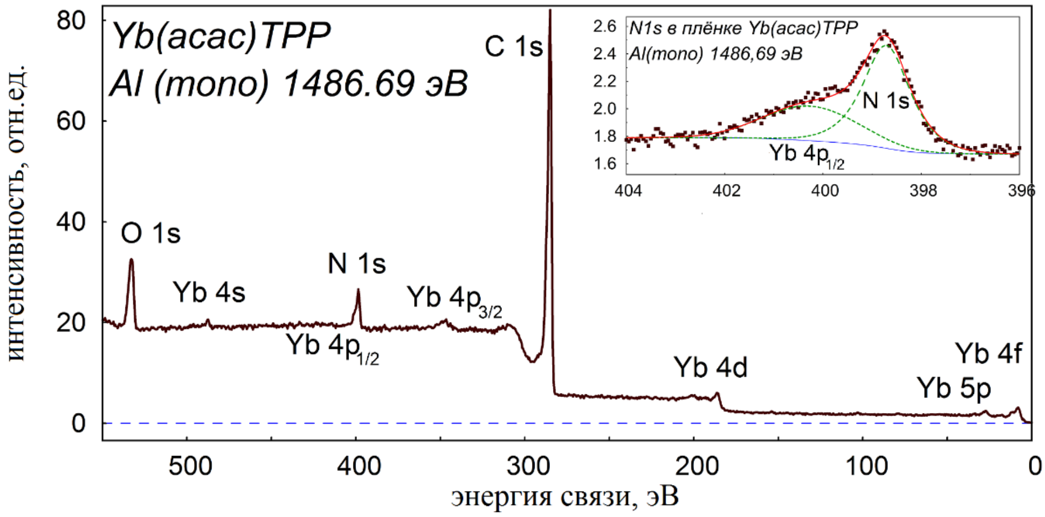

Figure 8. XPS spectrum of Yb(acac)TPP after thermal deposition.

[интенсивность, отн. ед. means Intensity, rel. units; в плёнке means in the film of; эВ means eV; в means in; энергия связи, эВ means Binding energy, eV]

A preliminary study showed that Yb(acac)TPPBr$_8$ undergoes partial destruction upon thermal impact. XPS spectra of the core Br3d level in Yb(acac)TPPBr$_8$ studied with the use of a Russian-German photoelectron line in BESSY-II (photon energy: 600 ev) (Figure 9) show a change of the Br3d line when heating from room temperature to 150°C. The obtained spectra distinctly show two states of bromine: the first state corresponds to bromine in the compound, and the second one, probably, to the atomic state of bromine. Further heating of the sample (Figure 9) results in an increase of the peak corresponding to the free state, which proves that thermal decomposition of the compound occurs [14].

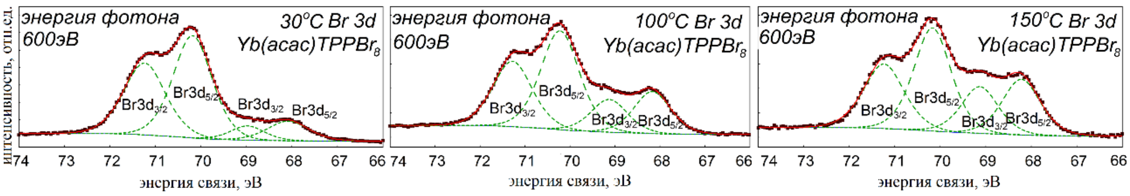

Figure 9. XPS spectrum of the Br3d region in Yb(acac)TPPBr$_8$ at 30, 100 and 150^{o}C *in situ*. [интенсивность, отн. ед. means Intensity, rel. units; энергия фотона 600эВ means Photon energy: 600 eV; энергия связи, эВ means Binding energy, eV]

In order to analyze the behavior of metalloporphyrins and tetraphenylporphyrin upon heating TPP and its complexes, such as TPPBr$_8$, Yb(acac)TPP and Yb(acac)TPPBr$_8$ were studied by thermogravimetry (Figure 10). In the course of the measurement samples were heated from 20–25 to 450°C, and then cooled to 50°C at a controlled rate.

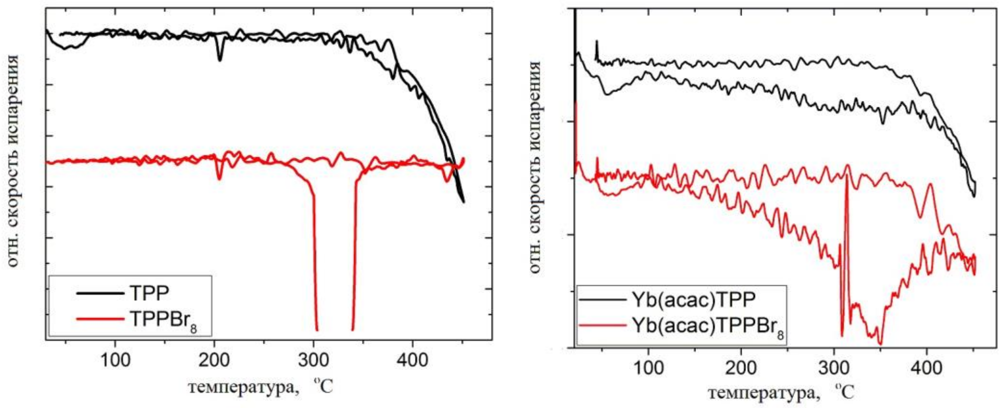

Figure 10. Dependence of relative evaporation rate (sample weight change) on temperature in case of TPP (upper curve), TPPBr$_8$ (lower curve) *(left)* and Yb(acac)TPP (upper curve), Yb(acac)TPPBr$_8$ (lower curve) (*right*). [отн. скорость испарения means Rel. evaporation rate; температура means temperature]

Because the results of X-ray photoelectronic spectroscopy show that only TPP and Yb(acac)TPP evaporate in vacuum congruently, and the other complexes do not, it can be assumed that heating results in the decomposition of the brominated compounds: TPPBr$_8$ and Yb(acac)TPPBr$_8$.

Note that in case of octabromo derivatives TPPBr$_8$ and Yb(acac)TPPBr$_8$ an abrupt jump of relative evaporation rate and its subsequent decrease are observed at a temperature over 300°C. Perhaps this is due to the compounds decomposition. Taking into account the fact that the TPPBr$_8$ curve at temperatures over 350°C differs from the TPP curve, it can be assumed that the macrocycle decomposition occurs rather than partial or complete elimination of the bromine atoms.

Unfortunately, the analysis of the thermogravimetry diagram of Yb(acac)TPPBr$_8$ does not allow to draw similar conclusions. For this purpose we studied the rest of the compound (from the crucible) by XPS after heating to 450°C followed by cooling (Figure 11).

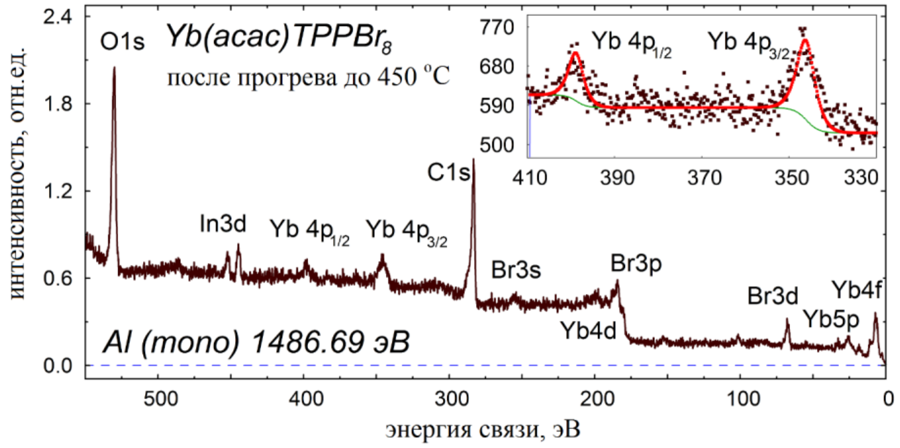

Figure 11. XPS spectrum of Yb(acac)TPPBr$_8$ after thermogravimetry (heating to 450^{o}C).
[интенсивность, отн. ед. means Intensity, rel. units; энергия связи, эВ means Binding energy, eV; после прогрева means after heating]

The analysis of the XPS spectrum of Yb(acac)TPPBr$_8$ after thermogravimetry (Figure 11) enables to draw a conclusion about the molecule decomposition into components. This is indicated by the weak signal of nitrogen, the peak of which does not exceed 5% of the peak at 390–400 eV, while the normal contribution is 55–60%. Because the central "nitrogen cavity", via which ytterbium acetylacetonate is bound to the macrocycle, is a characteristic feature of porphyrin compounds, it can be assumed that the metal complex undergoes decomposition.

Conclusion

Ytterbium acetylacetonate, the free bases of tetraphenylporphyrin and its octabromo and ytterbium complexes based on them were synthesized.

In the photoelectron spectra of the core level of N1s state of initial TPP and TPPBr$_8$, a distinct characteristic two-peak structure corresponding to the nitrogen atom in the pyrrole group (sp^3) and the aza-group (sp^2) are present. The existence of the central ytterbium atom in the metalloporphyrin results in more uniform redistribution of electron density between the nitrogen groups. In the XPS spectra of the studied ytterbium metalloporphyrins one broadened peak of N1s-states is observed. This indicates a small difference of binding energy of the pyrrole and aza nitrogen.

In the spectra of Yb4d states of the metalloporphyrin, an electronic structure with multiplet splitting and close energies of binding with ytterbium(III) oxide is observed. This indicates similar states of the ytterbium ion and confirms the trivalent state of the metal (Yb^{3+}) in Yb(acac)TPP and Yb(acac).

Studies on the thermal stability of TPP, $TPPBr_8$, Yb(acac)TPP and Yb(acac)$TPPBr_8$ by XPS and thermogravimetry in the temperature range 30–450°C upon heating in ultra-high vacuum showed the decomposition of $TPPBr_8$ and Yb(acac)$TPPBr_8$ after heating above 150°C and the stability of basic tetraphenylporphyrins.

Acknowledgment

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