

NEXAFS Study of Zinc Porphyrins Intercalated into  $V_2O_5$  XerogelVictor N. Sivkov,<sup>a@</sup> Galina S. Zabrodina,<sup>b</sup> Sergei V. Nekipelov,<sup>a</sup> Olga V. Petrova,<sup>a</sup> Elena A. Shchupak,<sup>b</sup> Denis V. Vyalikh,<sup>c</sup> and Sergei L. Molodtsov<sup>c</sup><sup>a</sup>Komi Science Center Ural Division RAS, 167982 Syktyvkar, Russia<sup>b</sup>G.A. Razuvaev Institute of Organometallic Chemistry RAS, 603950 Nizhniy Novgorod, Russia<sup>c</sup>Technische Universitat Dresden, D-01062, Dresden, Germany<sup>@</sup>Corresponding author E-mail: svn@dm.komisc.ru

For the first time the NEXAFS N1s- and C1s- spectra of composites on the basis of macrocyclic molecules - zinc meso-tetrakis(4-pyridyl)porphyrin, zinc meso-tetrakis(N-methylpyridinium-4-yl)porphyrin tetraiodide and  $V_2O_5 \cdot nH_2O$  xerogel were studied by a total electron yield method with using synchrotron radiation of Russian-Germany beamline at BESSY-II. These intercalation complexes are insoluble in water, stable and exhibit good electrochemical properties. The host-guest interaction leads to the great changes of NEXAFS N1s- and C1s-spectra of the synthesized composites as compared with pristine compounds spectra. The studies show the 2.1 eV blue shift energy position and great increase oscillator strength of the  $\pi$ -resonance in the NEXAFS N1s- spectra of pyridine cycle when ZnPor(Py)<sub>4</sub> intercalated into  $V_2O_5 \cdot nH_2O$  xerogel.

**Keywords:** NEXAFS, zinc porphyrin complexes, intercalation, vanadium pentoxide xerogel.

## Introduction

The unique properties of the 3d-transition metal porphyrins and related macrocycles have widely applications in various fields in science and technology.<sup>[1]</sup> One of the such important applications is incorporation of metal porphyrin into porous or layered materials. Intercalated compounds are a special family of materials formed by inclusion of guest species into the layered host lattice. The intercalation reactions involving layered host lattices and different kinds of guest materials have been most extensively studied, because of the structural flexibility and ability to adapt to the geometry of the intercalated guest species by free adjustment of the interlayer separation and wide applications of these compounds.<sup>[2]</sup>

The important examples of this class of materials are the intercalation compounds on the basis of porphyrins and their analogues due to catalytical, photocatalytical, photochemical, photophysical properties of the macrocyclic ring. The intercalation complexes possess better catalytic activity compared to the starting porphyrins due to the molecular distribution of porphyrins in solid matrix.

Vanadium pentoxide xerogel has been widely studied as the host matrix for intercalation compounds preparation.<sup>[3]</sup>

The materials based on the porphyrin derivatives intercalated into  $V_2O_5 \cdot nH_2O$  xerogel possess the high application potential as catalysts, sensors and modified electrodes. Physical and chemical properties of these systems should be dependent on orientation of porphyrin ring inside  $V_2O_5 \cdot nH_2O$  xerogel lattice and host-guest interaction. The synthesis and properties of intercalation compounds obtained by introduction of cationic forms of pyridyl substituted porphyrins from aqueous solutions

into  $V_2O_5 \cdot nH_2O$  xerogel have been previously described.<sup>[4]</sup> These intercalation complexes are insoluble in water (unlike the starting reagents), stable, and exhibit good catalytical and electrochemical properties. The X-ray diffraction data of these intercalation compounds show the increase of the interlamella distances of xerogel. The stacking of the lamellar structure is dependent on the orientation of metalloporphyrin between the  $V_2O_5$  layers. UV and IR-spectra indicate that the porphyrin derivatives in the composite material may be in the protonated form.

The aim of this work is to study the intercalation compounds based on the macrocyclic molecules of zinc meso-tetrakis(4-pyridyl)porphyrin (ZnTPyP), zinc meso-tetrakis(N-methylpyridinium-4-yl)porphyrin (ZnTMPyP), and  $V_2O_5 \cdot nH_2O$  xerogel (VPX) by the method of NEXAFS spectroscopy. The protonation of complexes should lead to the great changes of the electron density distribution in the porphyrin during intercalation and the great changes of near edge X-ray fine structure (NEXAFS) N1s- and C1s- spectra of the synthesized ZnTPyP-VPX, ZnTMPyP-VPX composites as compared with pristine compounds spectra. The NEXAFS spectroscopy is the available tool for the investigation both of the changes in porphyrin macromolecules and the TMPyP-xerogel interaction, because the NEXAFS-spectroscopy methods are characterized by atomic selectivity, dipole selection rules, fast response atomic composition and spatial conformation.<sup>[5]</sup>

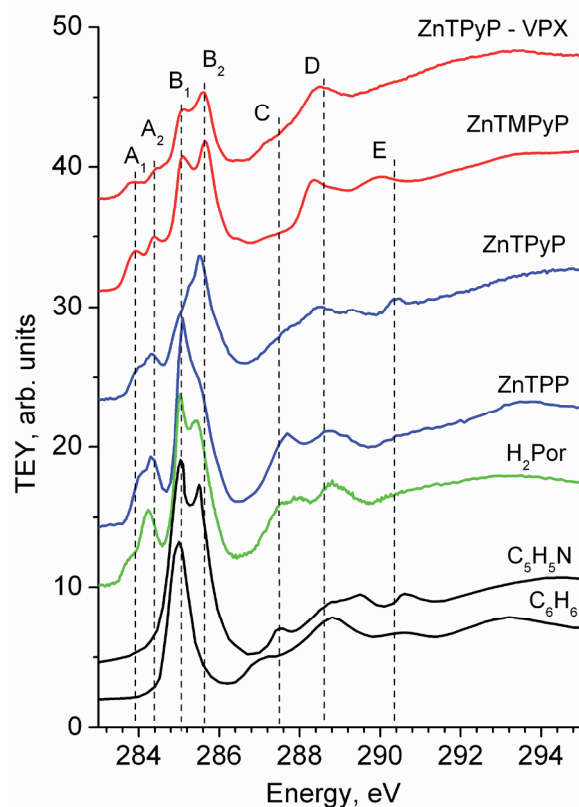
## Experimental

ZnTPyP-VPX and ZnTMPyP-VPX composite samples were produced by inclusion of cationic form of substituted porphyrins from aqueous solutions into  $V_2O_5 \cdot nH_2O$  xerogel. The gel was supplied onto glass plates with a brush in a regular layer and

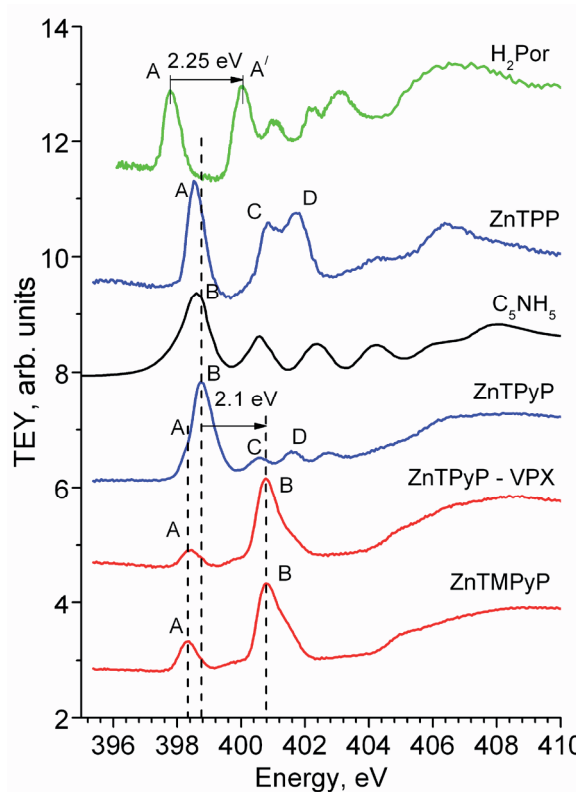
dried in air or in a vacuum.<sup>[4]</sup> The samples for the investigation by TEY (Total Electron Yield) method were prepared by the pressing compounds on the Cu metal surface. Additional Ti-films of the 160–210 nm thickness mounted onto Au-grid with small mesh were used for the effective suppression and the measurement of the second-order light and the VUV-stray radiation.<sup>[6]</sup> The incident photon flux ( $E = 280\text{--}450$  eV) was alternately measured using a TEY detector recording electron yield from the clean Au-photocathodes. Experiments were performed at BESSY-II using radiation from the Russian–German beamline. This dipole beamline was proven to be suitable for the measuring of absorption cross section in NEXAFS range of C1s- and N1s-edges.<sup>[7]</sup> The NEXAFS C1s- and N1s-spectra were acquired in a total electron yield mode. The resolution for the NEXAFS-measurements was varied from 80 to 100 meV.

## Results and Discussion

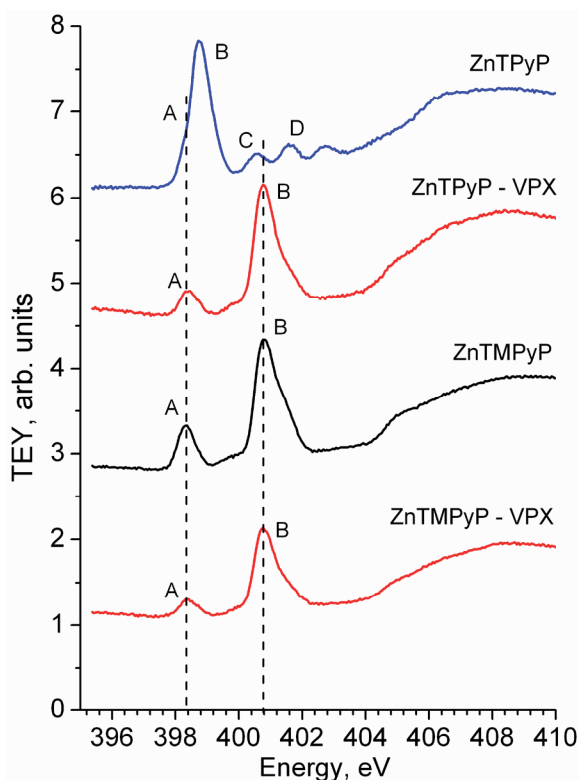
Figures 1 and 2 show NEXAFS C1s- and N1s-spectra of the composite ZnTPyP-VPX, pristine ZnTPyP, ZnTMPyP-VPX, H<sub>2</sub>P, ZnTPP studied in this work, and C<sub>6</sub>H<sub>6</sub> and C<sub>5</sub>NH<sub>5</sub> molecules, studied earlier.<sup>[8]</sup> At present NEXAFS C1s- and N1s-spectra of H<sub>2</sub>P and ZnTPP molecules are well known both experimentally and theoretically.<sup>[9–11]</sup> NEXAFS 1s-spectra obtained in present work well agree with these researches. The C1s-spectra fine structure elements of studied compounds consist of three groups: low peaks  $A_1$  and  $A_2$  (except molecules), high peaks  $B_1$  and  $B_2$  (except C<sub>6</sub>H<sub>6</sub>) and wide bands  $C$ – $E$ . In the spectra of benzene and pyridine there are no peaks  $A_1$  and  $A_2$ , assigned to C1s→ $\pi^*$  transitions in carbonic atoms of the flat porphyrin macrocycle, which consists of four pyrrole subunits bridged by four *meso*-carbon atoms. High peaks  $B_1$  (energy position at 285.0 eV in the benzene spectrum and 285.1 eV in spectra of the other compounds) and  $B_2$  (energy position at 285.6 eV in the composite spectra and protonated TMPyP and 285.4 eV in spectra of the other compounds) are assigned to C1s→ $\pi^*$  transitions in carbonic atoms of the aromatic rings of pyridine and benzene. The second absorption peak  $B_2$  reflects the electronic transitions in carbonic atoms neighbouring nitrogen atom. Wide bands  $C$ – $E$  are assigned to C1s→ $\sigma^*$  transitions. Figure 1 shows that the intensities of peaks  $A_1$  and  $A_2$  as against  $B_1$  and  $B_2$  are decreased going from the spectra of H<sub>2</sub>P and ZnTPP to the spectra of TMPyP without changing energy positions, what is, probably, connected with increasing number of carbon atoms in these compounds. The ZnTPP and TMPyP C1s-spectra look like a simple superposition of the other two, confirming that there is almost no interaction between the  $\pi$  states of the macrocycle and those of the phenyl and pyridyl groups, respectively. Observed differences in C1s-spectra of TMPyP and ZnTPyP-VPX composite cover the peak  $B_2$  intensity and the energy position variations are, probably, connected with the redistribution electronic change differs of nitrogen atom and neighbouring carbonic atoms in the pyridine cycle, which must occur in the protonated forms. From this point of view, it is interesting to look at the NEXAFS N1s-spectra. In Figure 2 the X-ray absorption spectrum at the nitrogen 1s-edge of studied compounds are presented. Taking into account the NEXAFS N1s-spectra characteristic features we can divide these compounds into three groups: (1) H<sub>2</sub>P; (2) ZnTPP, ZnTPyP and C<sub>5</sub>NH<sub>5</sub> molecule; (3) ZnTMPyP and composite ZnTPyP-VPX. The spectrum of H<sub>2</sub>P consists of two peaks -  $A$  (398.8 eV) and  $A'$  (400.05 eV) connected



**Figure 1.** NEXAFS C1s-spectra of the synthesized composite ZnTPyP-VPX, initial compounds ZnTPyP, ZnTMPyP, H<sub>2</sub>P, ZnTPP and molecules of C<sub>6</sub>H<sub>6</sub> and C<sub>5</sub>H<sub>5</sub>N.<sup>[8]</sup>



**Figure 2.** NEXAFS N1s-spectra of the synthesized composite ZnTPyP-VPX, initial compounds ZnTPyP, ZnTMPyP, H<sub>2</sub>P, ZnTPP and molecule of C<sub>5</sub>H<sub>5</sub>N.<sup>[8]</sup>



**Figure 3.** NEXAFS N1s-spectra of the synthesized composites ZnTPyP-VPX, ZnTMPyP-VPX and initial compounds ZnTPyP, ZnTMPyP.

with the electronic transitions from the N1s core level to the lowest unoccupied molecular orbital of the macrocycle  $\pi^*$  system in the nitrogen atoms (Mac N) and the protonated nitrogen atoms (Mac N-H), respectively. The chemical shift of 2.25 eV between these atoms ensues of the protonated nitrogen.<sup>[11]</sup> The NEXAFS N1s-spectrum of ZnTPP consists of peak A (398.4 eV) and doublet band C-D assigned to the transitions to the  $\pi^*$  states of the porphyrin macrocycle. In the pyridine spectrum the intensity peak B (398.6 eV), assigned to transitions to the  $\pi^*$  state of the pyridine ring, dominates. The shoulder A (398.3 eV) and high peak B (398.7 eV) in the ZnTPyP spectrum correspond to the peaks A and B in spectra of ZnTPP and pyridine, respectively. The presence of methyl group in  $\text{ZnP}(\text{Py}^+\text{Me})_4$  and the result in the NEXAFS N1s-spectra great changes are expressed in the blue shift energy positions of peak B. This effect is observed in the N1s-spectra of  $\text{ZnP}(\text{Py})_4$  intercalated into  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  xerogel, that makes it possible to suppose an existence of the protonated nitrogen atoms in the ZnTMPyP intercalated into xerogel. The fact, that the blue shift value (2.1 eV) in the composite N1s-spectrum well correlates with the shift in the  $\text{H}_2\text{P}$  N1s-spectrum (2.25 eV) due to nitrogen protonation. Figure 3 shows, that NEXAFS N1s-spectrum of ZnTMPyP

is identical to the NEXAFS N1s-spectra of the composite ZnTPyP-VPX. Thus, intercalation of these compounds into VPX does not reduce the additional protonation of nitrogen atom in pyridine groups.

## Conclusions

Using synchrotron radiation by NEXAFS spectroscopy methods we have investigated the C1s- and N1s-spectra of the composites ZnTPyP-VPX and ZnTMPyP-VPX. For the first time we have identified the NEXAFS N1s-absorption spectra modification (2.1 eV blue shift of the pyridine cycle  $\pi^*$ -resonance) when ZnTPyP molecule is intercalated into  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  xerogel. The investigation results show wide possibilities of NEXAFS spectroscopy methods for the protonated process studies of the macrocycle compounds and composites on its basis.

**Acknowledgements.** This work was supported by the Bilateral Program of the Russian-German Laboratory at BESSY II. We would like to thank Olga N. Suvorova, Aleksei I. Kirillov (G.A. Razuvaev Institute of Organometallic Chemistry RAS, Nizhny Novgorod) and D. Woehrl (Bremen University) for the given standard samples and for helpful discussion.

## References

1. *The Porphyrin Handbook* (Kadish K.M., Smith K.M., Guillard R., Eds.) San Diego, CA: Academic, 2000, Vol. 6, p. 131.
2. O'Hare D. In: *Inorganic Materials* (Bruce D.W., O'Hare D., Eds.) New York: John Wiley and Sons, 1991, p. 165.
3. Hagrman P.S., Finn R.C., Zubieta J. *Solid State Sci.* **2001**, 3, 745.
4. Suvorova O.N., Domrachev G.A., Shchupak E.A., Kundryatseva G.S., Kirillov A.I., Zaitsev A.A. *Russ. Chem. Bull.* **2009**, 58, 2233-2239.
5. Stoehr J. *NEXAFS Spectroscopy*. Berlin: Springer, 1992. 403 p.
6. Kummer K., Sivkov V.N., Vyalikh D.V., Maslyuk V.V., Blüher A., Nekipelov S.V., Bredow T., Mertig I., Mertig M., Molodtsov S.L. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, 80, 155433.
7. Gorovikov S.A., Molodtsov S.L., Follath R. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1998**, 411, 506-512.
8. Akimov B.H., Vinogradov A.S., Pavlychev A.A., Sivkov V.N. *Opt. Spectrosc. (USSR)* **1985**, 59, 206-211 [*Opt. Spektrosk.* **1985**, 59, 342-347 (in Russ.)].
9. Schmidt N., Fink R., Hieringer W. *J. Chem. Phys.* **2010**, 133, 054703.
10. Castellarin Cudia C., Vilmercati P., Larciprete R., Cepek C., Zampieri G., Sangaletti L., Pagliara S., Verdini A., Cossaro A., Floreano L., Morgante A., Petaccia L., Lizzit S., Battocchio C., Polzonetti G., Goldoni A. *Surf. Sci.* **2006**, 600, 4013-4017.
11. Polzonetti G., Carravetta V., Iucci G., Ferri A., Paolucci G., Goldoni A., Parent P., Laffon C., Russo M.V. *Chem. Phys.* **2004**, 296, 87-99.

Received 20.05.2011

Accepted 20.06.2011