

# Electronic structure and self-assembling processes in platinum metalloporphyrins: photoemission and AFM studies

A.I. Belogorokhov · S.I. Bozhko · A.N. Chaika ·  
A.M. Ionov · S.A. Trophimov · V.D. Rumiantseva ·  
D. Vyalikh

Received: 20 December 2007 / Accepted: 9 September 2008 / Published online: 14 October 2008  
© Springer-Verlag 2008

**Abstract** The main goal of this paper is to investigate the electronic structure of valence band and core levels as well as surface topography of pristine tetraphenylporphyrin and Pt-based compounds Pt-TPP(p-COOH<sub>3</sub>)<sub>4</sub>, Pt-TPP(m-OCH<sub>3</sub>)<sub>4</sub>, PtCl<sub>2</sub>-TPP(m-OCH<sub>3</sub>)<sub>4</sub> thin films. The electronic structure of various Pt-based metalloporphyrins which were investigated in dependence on their chemical structure and spectra were measured by high-resolution X-ray photoelectron spectroscopy (XPS) of valence band and Pt4f, Pt4d, C1s, O1s, N1s core levels. Results of atomic force microscopy (AFM) studies of topography and self-assembling processes in thin films of porphyrines are presented and discussed.

**PACS** 73.20.At · 79.60.Fr

The electronic structure and morphology of tetraphenylporphyrin (TPP) and Pt-based Pt-5,10,15,20-tetrakis-methoxycarbonylphenyl-TPP(p-COOCH<sub>3</sub>)<sub>4</sub>, Pt-TPP(m-OCH<sub>3</sub>)<sub>4</sub>; PtCl<sub>2</sub>-TPP(m-OCH<sub>3</sub>)<sub>4</sub> thin films, prepared by evaporation

under ultra high (UHV) and high vacuum (HV) onto Si(100) and mica substrates, were studied by atomic force microscopy (AFM) and photoelectron spectroscopy (PES).

The Pt-porphyrins were synthesized in benzonitrile with PtCl<sub>2</sub>(PhCN)<sub>2</sub> under nitrogen atmosphere [1].

The electronic structure and topography of tetraphenylporphyrin (TPP) and Pt-based Pt-TPP(p-COOCH<sub>3</sub>)<sub>4</sub>, Pt-TPP(m-OCH<sub>3</sub>)<sub>4</sub>, PtCl<sub>2</sub>-TPP(m-OCH<sub>3</sub>)<sub>4</sub> thin films were studied by PES and AFM. Samples were prepared by evaporation under UHV in situ and additionally by means of deposition from the CHCl<sub>3</sub> solution by self-assembling techniques onto Si(100), mica and Cu substrates. The surface of samples was cleaned for PES in situ by heating at 400 K, the pressure was about  $1 \times 10^{-9}$  mbar. The high-resolution PES (HRPES) studies of valence band (VB) and core levels were performed in the RBL BESSY II using photon energies of 120–600 eV at normal emission (total resolution was about 120 meV) and electron spectrometer ESCALAB-5 (Mg K<sub>α</sub>).

All elements of pristine TPP (analogous to Fig. 1(3)) but without radicals R) and metalloporphyrins (similar to [2–5]) were found in XPS spectra after moderate annealing in UHV. XPS spectra of N1s and C1s levels and VB spectra are shown in Figs. 2, 3. In TPP XPS spectra two peaks of N1s with binding energies of 399.8 and 397.8 eV were assigned to sp<sup>3</sup> and sp<sup>2</sup> nitrogen respectively (see Fig. 1(3)) according to reference [3]. In metalloporphyrins charge distribution is more uniform for N1s spectra of Pt<sup>2+</sup>-TPP(m-OCH<sub>3</sub>)<sub>4</sub> and other metalloporphyrins [2] and wide peak of N1s states reflects small difference between pyrrole- and aza-nitrogen in Pt-metalloporphyrins (Fig. 1(4)).

Different peaks at 285 and 286.2 eV which were seen in the C1s spectra are related to the main unequivalent C atoms in molecules (similar to data for TPP and phthalocyanines [3–5], aromatic and C–N–C groups). Pt4f<sub>7/2</sub> level is

---

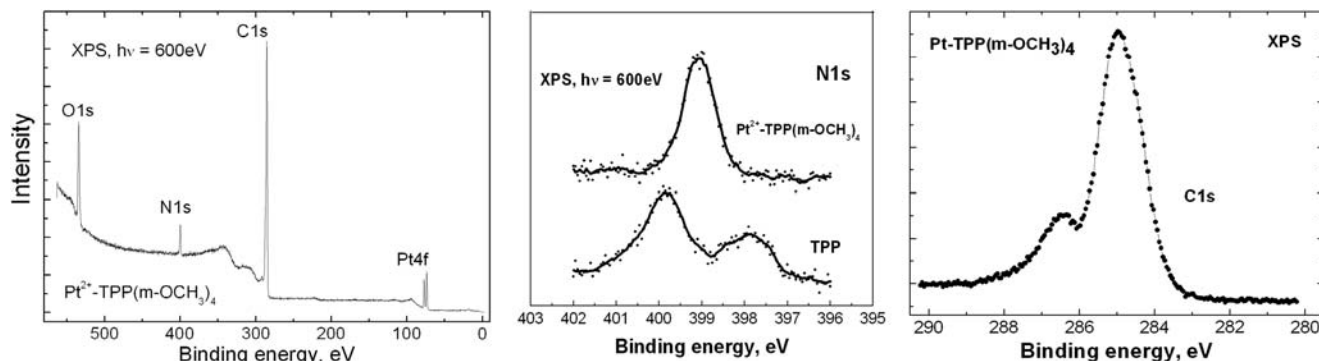
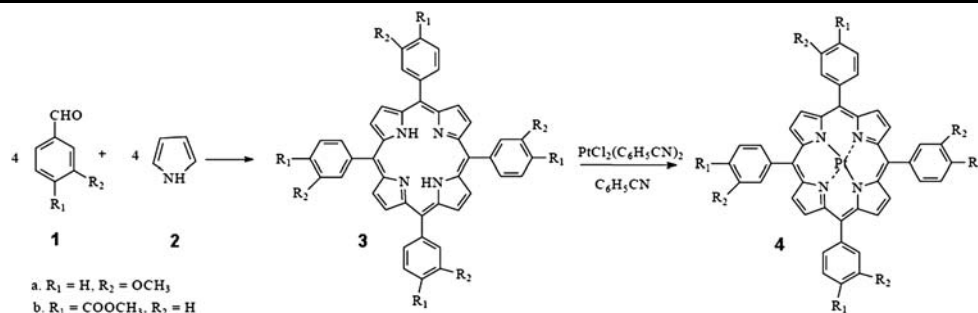
A.I. Belogorokhov  
Moscow State University, 119899, Moscow, Russia

S.I. Bozhko · A.N. Chaika · A.M. Ionov (✉) · S.A. Trophimov  
Institute of Solid State Physics, 142432, Chernogolovka, Russia  
e-mail: [ionov@issp.ac.ru](mailto:ionov@issp.ac.ru)  
Fax: +7-496-5249701

V.D. Rumiantseva  
Lomonosov State Academy of Fine Chemical Technology,  
119571 Moscow, Russia

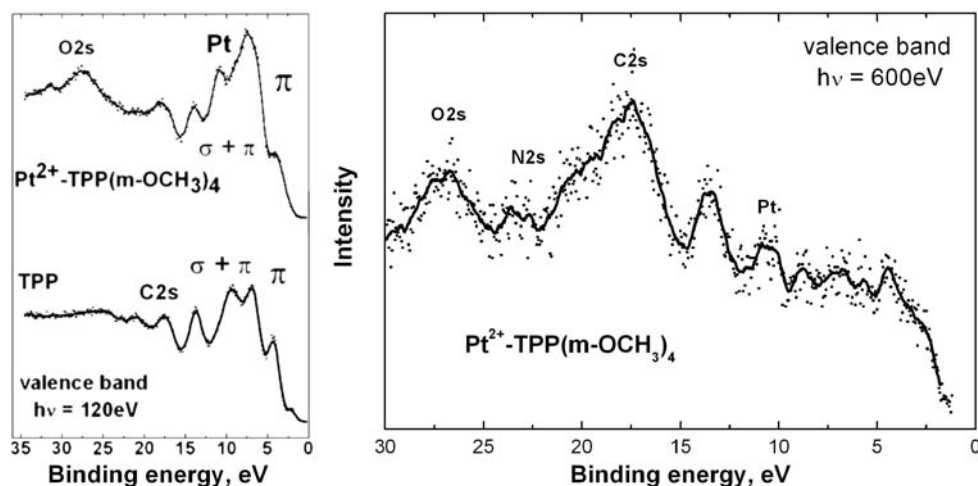
D. Vyalikh  
Technische Universität, Dresden, Germany

**Fig. 1** Scheme of synthesis of platinum complexes



**Fig. 2** XPS spectra of porphyrin compounds: *left panel*—raw XPS spectra of  $\text{Pt}^{2+}$ -TPP(m- $\text{OCH}_3$ )<sub>4</sub>, *centre and right panel*—XPS N1s and C1s spectra

**Fig. 3** VB spectra ( $h\nu = 120$  and 600 eV) of TPP and  $\text{Pt}^{2+}$ -TPP(m- $\text{OCH}_3$ )<sub>4</sub> compounds



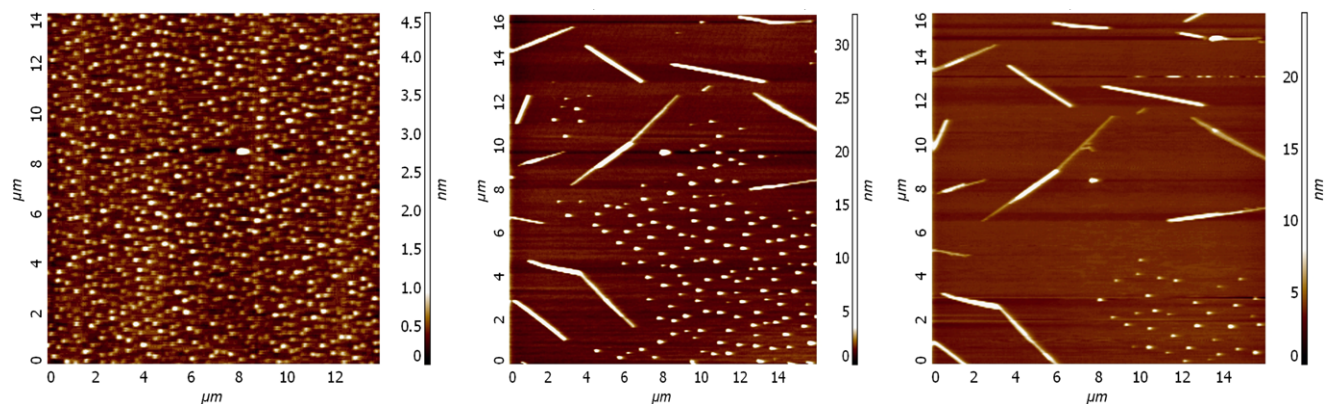
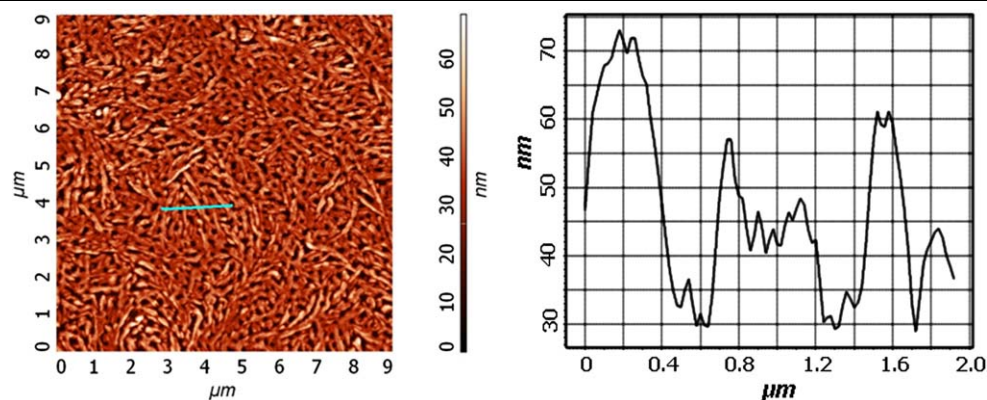
located at 73.3 eV with chemical shift 2.3 eV characteristic for divalent Pt, O1s level of ether ligands at about 533 eV.

The valence band is mainly formed by peaks corresponding to  $\pi$  (2–12 eV) and  $\sigma$  states (8–16 eV) of porphyrins macrocycles (analogous to Zn-TPP in reference [6]) and apparently can be reproduced by superposition of aromatic benzene and pyrrole spectra with HOMO derived features at 2 eV. The feature at 12 eV in Pt-TPP(m- $\text{OCH}_3$ )<sub>4</sub> is related with central metal ion of Pt. Semicore states of C2s ( $\sigma$ -type) and N2s in TPP and Pt-metalloporphyrins were at 18 and 23 eV, respectively, O2s at 27 eV in VB spectra. Accurate

positions and character of some orbitals in Pt-porphyrins will be studied using ARUPS and quantum-chemical calculations.

XPS and UPS studies have also demonstrated higher thermal stability of Pt-TPP(m- $\text{OCH}_3$ )<sub>4</sub> and  $\text{Pt}^{2+}$ -TPP(p- $\text{COOCH}_3$ )<sub>4</sub> in UHV comparing to  $\text{PtCl}_2$ -TPP(m- $\text{OCH}_3$ )<sub>4</sub>.

AFM studies of thin films structures prepared by HV deposition show that the structure of solid-phase films is determined by their chemical nature, supramolecular structure, and interaction with substrates. Typical AFM image of multilayer film of TPP on Si is presented in Fig. 4 (AFM ex-

**Fig. 4** Multilayer film of TPP on Si(100), *right panel*—profile**Fig. 5** Self-assembling in monomolecular films of tetraphenylporphyrin on mica. *Left*—initial state, *center*—after exposure of 15 min on air, *right*—after 45 min

periments were performed at air). Stable curved filamental structure was observed in multilayer film (10–12 ML) of TPP on Si(100) after deposition in high vacuum (substrate was at room temperature (RT)). Apparently in multilayered films porphyrin molecules are locked due to van der Waals forces between surface bound molecules forming stable curved structures.

The studies of formation and self-organization processes of porphyrin thin film structures after vacuum deposition (in accordance with the AFM data) show that the surface structure and morphology of thin film structures (columnar, planar, dendritic) is determined both by the character of macromolecules of porphyrin and metalloporphyrin as well as properties of substrates (silicon, mica). It was found that in monolayer films of porphyrins at air self-organization occurred with characteristic times of several tens of minutes (see for example Fig. 4), related with the reconstruction of low-dimensional macromolecular structures. Apparently for vacuum deposited porphyrins films, the morphology of the films is determined mostly by intermolecular  $\pi$ – $\pi$  interactions of porphyrin molecules and weak van der Waals interactions between aggregates and substrates.

It was shown that the substrates affect the deposited layers structure at earlier stages of the layer formation. Thus,

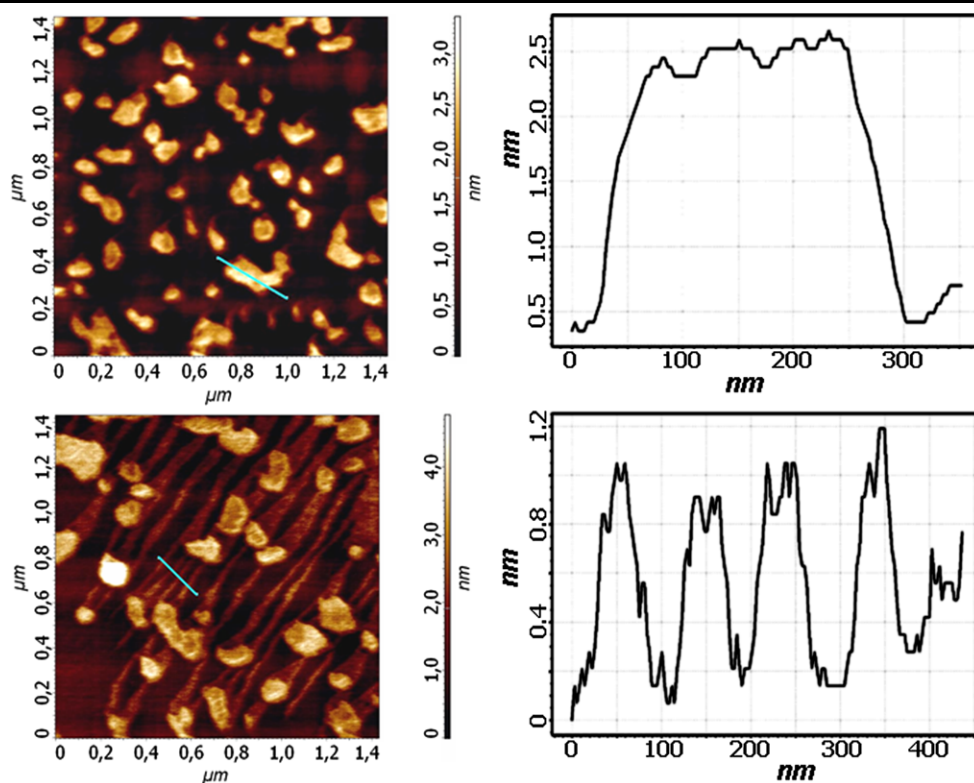
after deposition of TPP monomolecular film in HV, planar nanoislands with thicknesses of few molecules in-plane (0.5–2 nm) were formed (similar to data in [7]).

These films self-assemble at air into partially ordered large rod-shaped and flat supramolecular nanostructures on flat substrates, with an average size being in nanoscale, where the molecules are approximately parallel and cofacial to one another. AFM images (Fig. 5) demonstrate that at air islands transform to linear nanostructures with the height of 3–5 molecules oriented out-of-plane near perpendicular to substrate surface (mica).

Similar self-assembling processes were also observed for monomolecular films of Pt-TPP(p-COOCH<sub>3</sub>)<sub>4</sub>. Deposited films of Pt-TPP start to self-assemble through the tail structures (Fig. 6) formed by molecules oriented out-of-plane (edge-on) into big planar islands (not shown).

Note, that these self-assembling processes in deposited films of presented porphyrins occur seemingly under physico-chemical factors (photoexcitation, adsorption, charge transfer, might be AFM cantilever influence) which initiate formation processes of planar and linear nanostructures. In multilayered film of TPP at rather high deposition rate molecules probably are locked due to the van der Waals forces between surface bound molecules forming stable 3D curved

**Fig. 6** Self-assembling in monomolecular films of Pt-TPP(p-COOCH<sub>3</sub>)<sub>4</sub> on mica. *Top left* panel—*island structure*, *right*—*profile*, *bottom*—*after 1 h*, *tail structures and their profiles*



dendritic structures. After deposition of monolayered films the processes of self-assembling at air occurred with formation of low-dimensional structures of planar and columnar types. The similar results were reported in references [7–10] for chemically deposited films of porphyrins (phthalocyanines) and demonstrated that these molecules exhibit different assembling behavior on Si(111) and on a graphite surface, with TPP showing a greater tendency to self-assemble into ordered structures than phthalocyanines.

The XPS data show different atomic constituents in accordance with their states in molecules which can be related to the peaks appearing in the spectra. The UPS results give the position of the occupied states  $\pi$  and  $\sigma$  states in valence band of TPP and Pt-metalloporphyrins.

The structure of porphyrin films on differently polarized substrates—Si(100) and mica was studied by AFM. Analysis of AFM-images of deposited TPP and Pt-metalloporphyrins films shows that their structures change as the deposited porphyrin concentration grows. Results demonstrate that these molecules assemble into differently structured films on these substrates. In multilayered films the porphyrin molecules are locked due to van der Waals forces between surface bound molecules forming stable curved filamental structures. In monolayered films dynamic self-assembling processes have been observed on surfaces of porphyrins. The balance between intermolecular and interfacial forces

apparently defines the supramolecular organization and behavior of nanostructures where molecules oriented on-plane or out-of-plane (face-on or edge-on) on the surfaces.

**Acknowledgements** This work was supported by the Russian Academy Program “New Material and structures” and by the bilateral Program “Russian–German Laboratory at BESSY”.

## References

1. V.V. Vasiliev, S.M. Borisov, Y.O. Chubarova, V.D. Rumiantseva, J. Neorg. Chem. **48**(3), 455–461 (2003) (In Russian)
2. N. Nishimura et al., J. Electroanal. Chem. **473**, 75–84 (1999)
3. A. Ghosh, J. Moulder, M. Broering, E. Vogel, Angew. Chem. Int. **40**(2), 431–434 (2001)
4. H. Reisert, M. Knupfer, J. Fink, Surf. Sci. **515**, 491–498 (2002)
5. K. Park, A. Miller, K. Klier, R. Opila, J.E. Rowe, Surf. Sci. **529**, L285–L292 (2003)
6. A. Goldoni et al., Surface sciences and nanostructure. Elettra 73–78 (2006)
7. A. Solovieva, G. Vstovsky, S. Kotova, N. Glagolev, B.S. Zav’yalov, V. Belyaev, N. Erina, P. Timashev, Micron **36**, 508–518 (2005)
8. P. Bhyrappa, K.S. Suslick, J. Porphyr. Phthalocyanines **2**, 391–396 (1998)
9. S.B. Lei, J. Wang, Y.H. Dong, C. Wang, L.J. Wan, C.L. Bai, Surf. Interface Anal. **34**, 767–771 (2002)
10. K. Nakamura et al., Thin Solid Films **345**, 99–103 (1999)