SURFACE CHEMISTRY IN COMPLEX ORGANIC LAYERS

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Chemical reactions on surfaces can be followed in detail using X-ray photoelectron spectroscopy (XPS or ESCA), in particular in combination with scanning tunneling microscopy (STM). From the XPS binding energies of the adsorbate and substrate core levels, detailed information on the chemical composition, chemical state (e.g. oxidation state), adsorption sites, but also on the photoemission process itself can be derived. STM provides information on surface order and intramolecular conformation but also on the chemical state. Based on the understanding obtained for simple adsorbate systems, now complex molecular systems can be studied in great detail. One specifically interesting group of materials are metalloporphyrins. These metallotetrapyrrole complexes are versatile functional building blocks in many biological and biochemical processes. Moreover, there are several examples where such molecules were utilized in technical applications, retaining their highly functional nature within an inorganic framework. Examples include gas sensors, solar cells and catalysts. In this presentation the surface chemistry of porphyrins on metal and oxide substrates will be addressed. Specific topics are the interplay between porphyrin-substrate and porphyrin-porphyrin interactions, the role of the substrate, surface diffusion, and the synthesis of metalloporphyrin monolayers by direct metalation of free base porphyrins.[1-7]

Keywords: Porphyrins; Metalation; XPS; STM

References

[1] S. Ditze, M. Stark, M. Drost, F. Buchner, H.-P. Steinrück, H. Marbach, *Activation energy for the self-metalation reaction of 2H-tetraphenylporphyrin on Cu(111)*, Angew. Chem. Int. Edition 51 (2012) 10898.

[2] M. Röckert, M. Franke, Q. Tariq, S. Ditze, M. Stark, P. Uffinger, D. Wechsler, U. Singh, J. Xiao, H. Marbach, H.-P. Steinrück, O. Lytken, *Coverage- and Temperature-dependent Metalation and Dehydrogenation of Tetraphenylporphyrin (2HTPP) on Cu(111)*, Chem. Eur. J. 20 (2014) 8948.

[3] M. Stark, S. Ditze, M. Lepper, L. Zhang, H. Schlott, F. Buchner, M. Röckert, M. Chen, O. Lytken, H.-P.Steinrück, and H. Marbach, *Massive conformational changes during thermally induced self-metalation of 2H-Tetrakis-(3,5-di-tert-butyl)-phenyl-porphyrin on Cu(111),* Chem. Commun. 50 (2014) 10225.

[4] M. Röckert, M. Franke, Q. Tariq, H.-P. Steinrück and O. Lytken, *Evidence for a Precursor Adcomplex During the Metalation of 2HTPP with Iron on Ag(100),* Chem. Phys. Lett. 635 (2015) 60.

[5] M. Franke, F. Marchini, H-P Steinrück, O. Lytken, F. J. Williams, *Surface Porphyrins Metalate with Zn Ions from Solution*, J. Phys. Chem. Lett. 6 (2015) 4845-4849

[6] J. Schneider, M. Franke, M. Gurrath, M. Röckert, T. Berger, J. Bernardi, B. Meyer, H.-P. Steinrück, O. Lytken, O. Diwald, *Porphyrin Metalation at MgO Surfaces: a Spectroscopic and Quantum Mechanical Study on Complementary Model Systems*, Chem. Eur. J. 22 (2016) 1744-1749

[7] M. Franke, F. Marchini, N. Jux, H.-P. Steinrück, O. Lytken, F. J. Williams, *Zinc Porphyrin Metal Center Exchange at the Solid-Liquid Interface,* Chem. Eur. J. (in press)

CHEMISORPTION OF EXCHANGE-COUPLED METAL COMPLEXES ON GOLD VIA AMBIDENTATE CARBOXYLATO LIGANDS

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A novel strategy for the fixation of redox-active dinickel(II) complexes with high-spin ground states to gold surfaces was developed. The dinickel(II) complex $[Ni_2L(Cl)]ClO_4$ (where L represents a macrocyclic ligand) was reacted with ambidentate 4-(diphenylphosphino)benzoate (dppba) or 4-mercaptobenzoate (mba) coligands to form the carboxylato-bridged complexes $[Ni_2L(dppba)]^+$ (**2**) and $[Ni_2L(mba)]^+$ (**3**), which can both be isolated as perchlorate or tetraphenylborate salts. The auration of the complexes was probed on a molecular level, by reaction with AuCl or $[AuCl(PPh_3)]$, which leads to the monoaurated $Ni^{II}_2Au^I$ complexes $[Ni^{II}_2L(dppba)Au^ICl]ClO_4$ (**4**) and $[Ni^{II}_2L(mba)Au^IPPh_3]^+$ (**5**), respectively. The bridging thiolate-functions of the N_6S_2 macrocycle are deeply buried and are unaffected/unreactive under these conditions. All complexes were fully characterized by ESI mass spectrometry, IR and UV/Vis spectroscopy, X-ray crystallography, cyclic voltammetry, SQUID magnetometry and HF-ESR spectroscopy. Temperature dependent magnetic susceptibility measurements reveal a ferromagnetic coupling between the two Ni(II) ions in **2**-**5** with J values ranging from 15 - 23 cm^{-1}. HF-ESR measurements yield a negative axial magnetic anisotropy ($D < 0$) which implies a bistable (easy axis) magnetic ground state. The binding of the $[Ni_2L(dppba)]ClO_4$ complex to gold was ascertained by four complementary surface analytical methods: contact angle measurements, atomic force microscopy, X-ray photoelectron spectroscopy and spectroscopic ellipsometry. The results indicate that the complexes are attached to the Au surface via coordinative Au-P (or Au-S) bonds in a monolayer.

Keywords: Macrocyclic Ligands / High-Spin Molecules / Chemisorption / Ambidentate Phosphorus Ligands / Gold / Surface Complex

References

[1] J. Lach, A. Jeremies, D. Breite, B. Abel, B. Mahns, M. Knupfer, V. Matulis, O. A. Ivashkevich, B. Kersting *Inorg. Chem.* 53, (2014) 10825-10834
[2] M. Golecki, J. Lach, A. Jeremies, F. Lungwitz, M. Fronk, G. Salvan, D. R. T. Zahn, J. Park, Y. Krupskaya, V. Kataev, R. Klingeler, B. Büchner, B. Mahns, M. Knupfer, P. F. Siles, O. G. Schmidt, A. Reis, W. R. Thiel, D. Breite, B. Abel, B. Kersting, *Chem. Eur. J.* 19 (2013), 7787-7801

GROWTH, INTERACTION PHENOMENA AND PHASE DIAGRAM OF HETEROMOLECULAR ADSORBATES ON METAL SURFACES: THE MODEL SYSTEM PTCDA+CUPC/AG(111)

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Interfaces between organic semiconductors and metals have been investigated intensively in order to improve and develop future electronic devices. In this context the formation of molecular blends (i.e., heteromolecular layers containing at least two different types of molecules, usually charge donors und acceptors) on metal surfaces is of great interest. In this context, we have so far investigated structural and electronic properties of prototypical systems (PTCDA, NTCDA and several metal-Phthalocyanines on noble metal surfaces) using LEEM/PEEM, LEED, STM, NIXSW, ARPES, orbital tomography and STS.

Here we report a novel thermodynamic phase diagram for molecular blends formed by PTCDA+CuPc on Ag(111). In the submonolayer regime, two homo- and three heteromolecular ordered structures occur with different stoichiometry. Large eutectic regions exist in the phase diagram, caused by the opposite intermolecular interaction of the components – repulsive for CuPc, attractive for PTCDA. We find that the repulsive species cause the formation of a 2D lattice gas, the density of which determines the stability of all other phases. Critical values of the gas-phase density are the basis for understanding this constant-volume phase diagram that perfectly describes our experimental observations. We envisage the general validity of this type of phase diagram for binary systems containing gas-like phases.

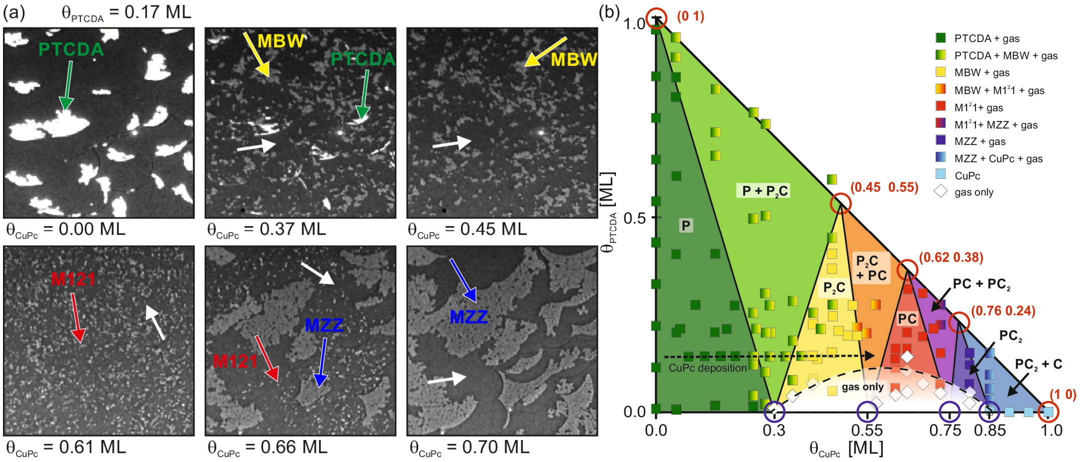

Fig. 1. (a) Bright-field LEEM images recorded during deposition: Initially, the Ag(111) surface is covered by 0.17 ML PTCDA (upper left image). Subsequently, 0.7 ML CuPc were deposited, as shown by the following five LEEM images. The original PTCDA islands (marked by green arrows) are sequentially transformed to MBW (yellow), M121 (red) and MZZ islands (blue), according to the stoichiometry sequence. (b) Phase diagram for PTCDA/CuPc heteromolecular submonolayer structures at 300K: Experiment and thermodynamic model. Colored areas and data points mark the regimes of pure and eutectic phases as obtained from model and experiment, respectively. A dotted arrow indicates the path of the experiment shown in (a). The model is based on more than 20 LEEM experiments with different initial coverages. Abbreviations: P = PTCDA, C = CuPc; Sequence and stoichiometry of the phases: PTCDA (P) – MBW (P2C) – M121 (PC) – MZZ (PC2) – CuPc (C).

Keywords: metal-organic interfaces, molecular blends, phase diagram, LEEM/PEEM

NOVEL INTERFACE-INDUCED ELECTRONIC AND SPIN STATES REVEALED BY SPIN-RESOLVED SCANNING TUNNELING SPECTROSCOPY

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Recently, exotic states of ultrathin films resulting from interfacial interactions have become of great interest in various fields of nanoscience research. As first example, nanoscale magnetic knots, called skyrmions, will be discussed which represent novel types of localized non-collinear spin textures offering great potential for future energy-efficient magnetic memory and logic devices [1]. The twisting in the skyrmions' magnetization profile leads to a gain in energy with respect to a homogeneously magnetized, ferromagnetic state. As a result of this magnetization twisting, skyrmions have non-trivial topological properties. The energetics of skyrmionic states in ultrathin films is explained by the interfacial Dzyaloshinskii-Moriya interaction [2] being relevant in material systems exhibiting large spin-orbit coupling and a lack of inversion symmetry. By using atomic-resolution spin-polarized scanning tunneling microscopy (SP-STM) and spectroscopy (SP-STS) [3] we have shown that magnetic skyrmions in ultrathin film systems can be as small as one nanometer in diameter [4] and that their properties can largely be tuned by the choice of the substrate and overlayer materials [5,6]. By locally injecting spin-polarized electrons from an atomically sharp SP-STM tip, we are able to write and delete individual skyrmions one-by-one, making use of spin-transfer torque exerted by the injected high-energy spin-polarized electrons [5]. Alternatively, individual skyrmions can be created and deleted by local electric fields, which can be of great advantage in view of energy-saving skyrmionic device concepts.

As second example, we will focus on interfacial superconductivity in novel types of heterostructures. Here, we present an SP-STS study of ultrathin $FeTe_{1-x}Se_x$ ($x = 0, 0.5$) films grown on prototypical Bi-based bulk topological insulators. We observe fully developed U-shaped superconducting gaps in $FeTe_{0.5}Se_{0.5}$ layers of one unit cell (UC) thickness with a transition temperature (Tc) of ~11 K, close to the one of the corresponding bulk system (Tc ~ 14.5 K). Surprisingly, we also find clear evidence for superconductivity up to Tc ~ 6 K for one UC thick FeTe layers grown on Bi_2Te_3 substrates, in contrast to the non-superconducting FeTe bulk compound which exhibits bicollinear AFM order in a wide temperature range up to 70 K. Even more surprisingly, detailed investigations of the atomic-scale spin-resolved local density of states by SP-STS reveal that superconductivity in one UC of FeTe grown on Bi_2Te_3 appears to spatially coexist with bi-collinear AFM order. This finding opens novel perspectives for theoretical studies of competing orders in Fe-based superconductors as well as for experimental investigations of exotic phases in heterostructures of topological insulators and superconducting layers.

References

[1] A. Fert et al., Nature Nanotechnology 8, 152 (2013).
[2] A. A. Khajetoorians et al., Nature Commun. 7, 10620 (2016).
[3] R. Wiesendanger, Rev. Mod. Phys. 81, 1495 (2009).
[4] S. Heinze et al., Nature Physics 7, 713 (2011).
[5] N. Romming et al., Science 341, 6146 (2013).
[6] N. Romming et al., Phys. Rev. Lett. 114, 177203 (2015).