

CPP 41: Organic Thin Films, Organic-Inorganic Interfaces I (joint session DS/CPP)

Time: Tuesday 9:30–11:00

Location: CHE 91

CPP 41.1 Tue 9:30 CHE 91

Shape controlled assembly of carboxylic acids: intercalation into molecular nanotunnels — RODRIGO ORTIZ DE LA MORENA¹, ANDIKA ASYUDA², HAO LU², HANNAH AITCHISON¹, KELLY TURNER¹, STEPHEN M. FRANCIS¹, MICHAEL ZHARNIKOV², and MANFRED BUCK¹ — ¹EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St Andrews KY16 9ST, United Kingdom — ²Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany

Binary self-assembled monolayers (SAMs) combining a Y-shaped aromatic carboxylic acid (CA), 1,3,5-benzenetribenzoic acid (H3BTB), and a cage-type alicyclic CA, adamantane CA (AdCA), were prepared by molecular adsorption from solution on Au substrates modified by underpotential deposition of Ag. These SAMs exhibit a pronounced dependence of their structure on the assembly protocol. Exposing an AdCA SAM to H3BTB results in the disordered arrangements. In contrast, exposing an H3BTB SAM to AdCA doesn't seemingly affect the highly regular row structure of the native H3BTB layer, with no signs (STM) of AdCA adsorption. However, spectroscopic analysis reveals its presence, suggesting that the AdCA molecules are hidden in the nanotunnels of the H3BTB monolayer. Additional evidence for this hypothesis is provided by appearance of densely packed and highly ordered AdCA monolayer upon local removal of H3BTB. Formation of such a compact layer is explained by expulsion of AdCA from the H3BTB nanotunnels of the surrounding intact mixed SAM, driven by release of stress in the nanotunnels built up when AdCA is intercalated.

CPP 41.2 Tue 9:45 CHE 91

Reestablishing odd-even effects in anthracene-derived monolayers by introduction of a proper symmetry — CHRISTOPH PARTES¹, ERIC SAUTER², MICHAEL GÄRTNER¹, MARTIN KIND¹, ANDIKA ASYUDA², MICHAEL BOLTE¹, ANDREAS TERFORT¹, and MICHAEL ZHARNIKOV² — ¹Institut für Anorganische und Analytische Chemie, Universität Frankfurt, 60438 Frankfurt, Germany — ²Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany

A series of anthracene[2,3-d]oxazolyl-2-alkylthioacetates (AOx_nCnSAC) with n = 2-6 methylene groups in the alkyl chain were designed and synthesized to investigate the influence of the substitution along the long axis of the molecule on the structural behavior of the respective self-assembled monolayers (SAMs) on Au(111). While in previous work anthracene-terminated alkanethiols, in which the alkyl group was attached to the off-axis 2-position of the acene, showed an exceptionally small influence of the number of methylene groups (n) in the aliphatic linker, the new system exhibits a strong dependence of almost all monolayer properties on the length of the aliphatic linker, with the parity of n being the decisive parameter - so-called odd-even effects. The high quality and well-defined character of these SAMs, along with a low band gap of only 3.0 eV, make them relevant for application in organic and molecular electronics.

CPP 41.3 Tue 10:00 CHE 91

Exploring Electron Beam Induced Processing on Porphyrin Multilayers for the Fabrication of Nanostructured Ultrathin Membranes — CHRISTIAN PREISCHL, ELIF BILGILISOY, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II Friedrich-Alexander Universität Erlangen-Nürnberg

We investigate two gas-assisted electron beam lithography methods, i.e. Electron-Beam-Induced-Deposition and Electron-Beam-Induced-Surface-Activation (EBISA) on porphyrin multilayers. In EBISA, a surface is irradiated by a focused electron beam, resulting in an activation of the exposed area. The activated areas can then lead to the decomposition of suitable precursor gases.^[1] Here we show that EBISA on thin layers of a free-base porphyrin (2HTPP) is compatible with the precursors Fe(CO)₅ and Co(CO)₃NO^[2]. Remarkably, the latter exhibited no EBISA-reactivity on other activated organic substrates like Self-Assembled-Monolayers or Surface-Anchored Metal-Organic Frameworks^[3]. We also demonstrate that thin layers of 2HTPP can be cross-linked to form a 2D carbon membrane via low energetic electron irradiation. This membrane is stable enough to transfer the metallic nanostructures onto any desirable substrate.

^[1] H. Marbach, *Appl. Phys. A* 117 (2014) 987 ^[2] M. Drost et al., *Small Methods* 1 (2017) 1700095 ^[3] M. Drost et al., *ACS Nano* 12

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CPP 41.4 Tue 10:15 CHE 91

Fabrication of metallic nanostructures via FEBIP on top of ultrathin organic membranes — ALEXANDER WOLFRAM, CHRISTIAN PREISCHL, ELIF BILGILISOY, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander Universität Erlangen-Nürnberg, GER

We report a novel method to fabricate ultrathin organic membranes with metallic nanostructures. In a first step, clean iron nanostructures were prepared on a self-assembled-monolayer (SAM) of 1,1',4',1''-terphenyl-4-thiol (TPT) via Electron-Beam-Induced-Deposition (EBID) by using Fe(CO)₅ as precursor.^[1] In a next step, the SAM is converted into a carbon nanomembrane (CNM) by using low energetic electron-induced crosslinking.^[2] In a third step, the membrane was then transferred onto SiO₂ or a TEM grid. We demonstrate that the nanostructures maintain their shape and the membrane remains intact during the transfer. In this way, metallic nanostructures on a free-standing CNM can be fabricated. We also show the influence of the underlying substrate (Ag or Au) of the SAM and the associated wet chemical process on the appearance of the transferred nanostructures.

^[1] M. Walz et al., *Angew. Chem. Int. Ed.*, 49 (2010) 4669 ^[2] A. Turchanin, A. Götzhäuser, *Advanced Materials*, 28 (2016) 6075.

CPP 41.5 Tue 10:30 CHE 91

Interfaces Between Tetraphenylporphyrin and Low-Work Function Metals: Interphase Formation Studied with HAXPES — MAIK SCHÖNIGER, STEFAN R. KACHEL, JAN HERRITSCH, PHILIPP SCHRÖDER, CLAUDIO K. KRUG, MARK HUTTER, and J. MICHAEL GOTTFRIED — Fachbereich Chemie, Philipps-Universität Marburg, Germany

Fabrication of organic electronic devices often involves the electrical contacting of organic semiconductors by vapor deposition of metals, resulting in the formation of metal-organic interfaces. These interfaces are crucial for the device's performance in terms of e.g. charge-carrier injection. However, especially metals with low work function can diffuse into and react with the organic material, leading to extended interphases consisting of the reaction products. The question then is: How thick is the formed interphase? As well-defined model systems, we investigated metalloporphyrin (M_xTPP) interphases formed through reaction of tetraphenylporphyrin (H₂TPP) with different vapor-deposited metals M, including earth alkalines (Mg, Ca) and the alkali metal Li. The non-destructive depth-profiling technique of choice is hard X-ray photoelectron spectroscopy (HAXPES), because H₂TPP and M_xTPP can be distinguished by their N 1s signals. Compared to earlier work with Fe and Co, Mg and Ca show increased reaction depths up to few nanometers. In the case of Li, complete reaction to Li₂TPP was observed in a 24 nm thick H₂TPP film. TPD-MS results showed that even thicker H₂TPP layers fully react.

CPP 41.6 Tue 10:45 CHE 91

Extended Interphase Formation at a Metal/Organic Interface: Lithium on Tetraphenylporphyrin — STEFAN RENATO KACHEL, MAIK SCHÖNIGER, JAN HERRITSCH, PHILIPP SCHRÖDER, MARK HUTTER, and J. MICHAEL GOTTFRIED — Fachbereich Chemie, Philipps-Universität Marburg, Germany

Porphyrins are versatile model compounds for organic semiconductors (OSC) in application-related studies of metal/organic interfaces. The properties of such interfaces strongly influence the performance of organic electronic devices. To study processes at the interface between an OSC and a low work-function metal, lithium was deposited onto tetraphenylporphyrin (H₂TPP) layers and the product composition was analyzed with temperature-programmed desorption mass spectrometry (TPD-MS) and X-ray photoelectron spectroscopy (XPS). With sufficient amounts of Li, we found complete conversion of H₂TPP into dilithium tetraphenylporphyrin (Li₂TPP). The depth range of this reaction exceeds several 10 nm, contrasting previous findings for transition metals. Even a 50 nm thick layer of H₂TPP fully reacted with an excess of Li. For substoichiometric amounts of Li, singly metalated LiHTPP was found. This study shows that the metal/organic interface can be very diffuse with a thick reacted interphase layer separating the metal from the pristine OSC.