Surface Science Day 6

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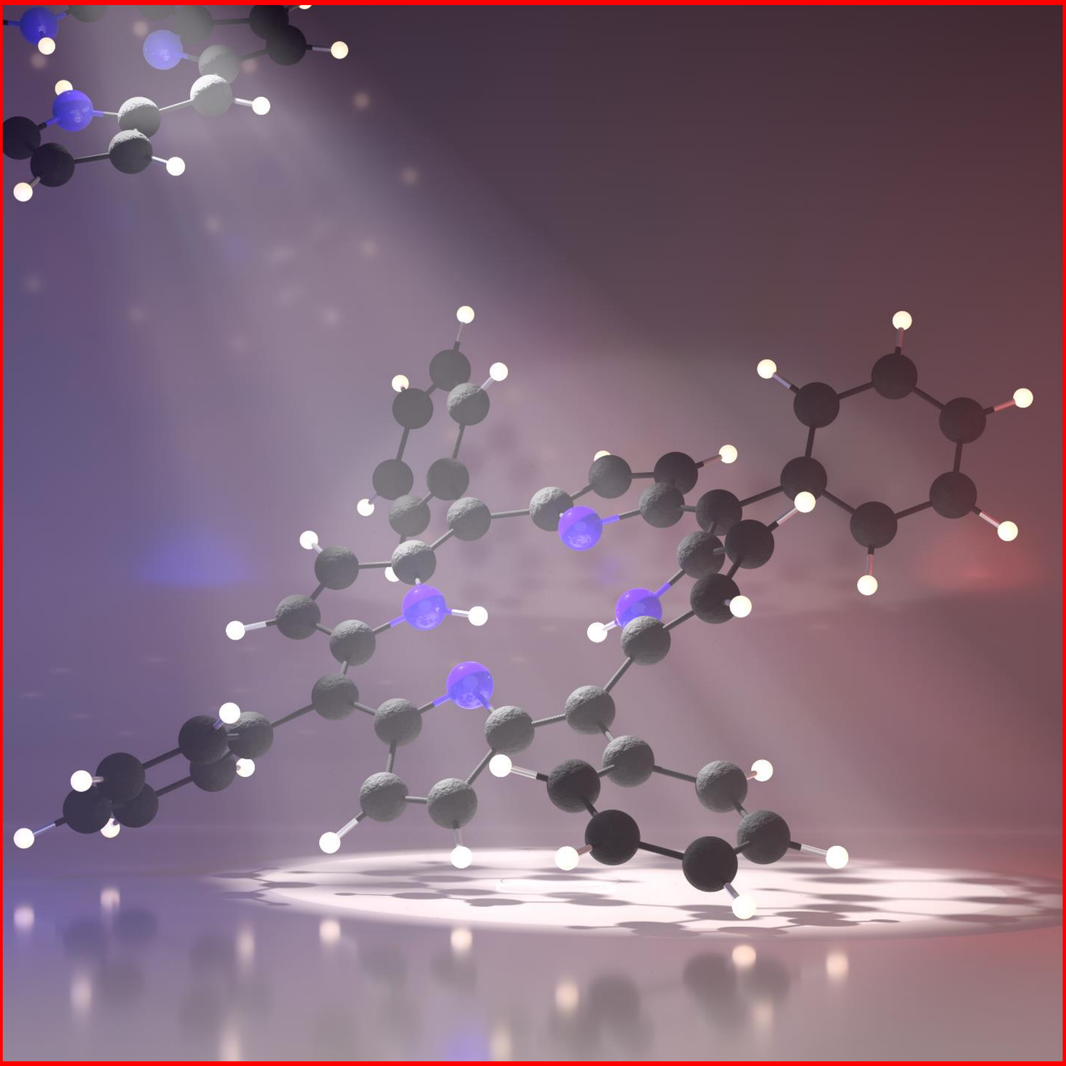
University of Nottingham



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Invited Talks

Determining the structure of 2D-materials with X-ray standing waves

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Two dimensional materials have grown significantly in importance over the last two decades. However, the term “two dimensional” is a misnomer for almost all such materials as there is always a degree of three-dimensionality due to the interaction of the material with its supporting substrate. How two dimensional a film is, thus, an interesting question and is one that can be neatly resolved by quantitative structural measurements. X-ray standing waves is the foremost method for performing such quantitative measurements, and herein, I will introduce the technique and provide several key examples into how these structural measurements address the question of just how two dimensional a two dimensional material is.

Intramolecular force mapping – from 5K to 293K

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The last decade has seen a dramatic improvement in our ability to characterize surfaces at the atomic scale via scanning probe microscope (SPM) techniques. In particular, non-contact atomic force microscopy (NC-AFM) is now routinely capable of obtaining sub-molecular resolution, readily resolving the carbon backbone structure of planar organic molecules adsorbed on metal substrates in real space [1]. These developments have arisen in part due to the now routine combination of scanning tunneling microscopy (STM) and NC-AFM into the same instrument, operation at cryogenic temperatures, and the controlled functionalization of the scanning probe tip by a carbon monoxide (CO) molecule or similar known passivating moiety.

In this talk, I will outline the conditions required to perform sub-molecular characterization with intramolecular resolution [2], and highlight recent developments made in our group in the field of high-resolution NC-AFM of single molecules with a focus on the extension of sub-molecular force mapping experiments to a much wider range of experimental conditions than previously thought possible [3,4].

[1] L. Gross, L., et al. Science,325, (5944),1110–1114. (2009).
[2] A. Sweetman, S.P. Jarvis, et al., Nature Communications 5, 3931 (2014).
[3] T. Brown et al. ACS Nano 2023, 17, 2, 1298–1304
[4] T. Brown et al. Communications Chemistry volume 7, Article number: 8 (2024)

May the dispersion force be with you:
Ab initio predictions of metastable surface nanostructures and 2D materials

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In a Density Functional Theory galaxy not so far from you, the accurate prediction of the structure, stability, and electronic properties of hybrid organic-inorganic interfaces and organic-metallic thin films remains a challenging task. Long-range dispersion interactions are often dominant forces. At the same time, when chemical bonds form at the surface, localized molecular electronic levels couple with a continuum of electrons in the substrate, leading to charge rearrangements at the interface. The interplay between these effects determines measurable level alignment, dynamical reaction outcomes and surface morphology. By understanding these effects from first principles, we advance our ability to design nanostructures and their properties from the bottom up.

In this talk, I will show how state-of-the-art electronic structure theory, surface spectroscopy simulations, and molecular dynamics simulations at surfaces provide atomic-scale insights needed to interpret diffraction, spectroscopy, and imaging measurements at surfaces for a variety of systems ranging from self-assembled two-dimensional donor-acceptor networks [1], bottom-up design of topological defects in graphene, [2] to single atom and molecule manipulation. [3]

[1] Blowey et al., ACS Nano 14 (2020): 7475–7483; Sohail et al, J. Phys. Chem. C 127 (2023).
[2] Klein et al., J. Phys. Chem. C 123, 29219-29230 (2019); Chemistry of Materials 32, 1041-1053 (2020); ChemPhysChem 22, 1065-1073 (2021)
[3] Knol et al., Science Advances 7 (2021); Bolat et al., Nature Communications 15, 2259 (2024)

A Facility for the Fabrication of 2D Material Heterostructures in Ultra-High Vacuum

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The development of deterministic stacking techniques as a means to fabricate so-called van der Waals (vdW) heterostructures during the last decade has opened the door to huge advances in the understanding of surface and interface physics in two-dimensional (2D) systems. Nevertheless, there still remain several obstacles that must be overcome that impede interface quality and limit the active area of devices. One of the main issues still to be resolved is the unwanted incorporation of contaminant hydrocarbons and atmospheric water into the device layers which typically manifest as 'bubbles' in heterostructures. Efforts to mitigate these such as the use of Ar/N_2 gloveboxes, low-residue tape during exfoliation and thermal annealing still do not eliminate the bubbles and the use of polymeric films (e.g. PMMA) to manipulate and deterministically place 2D material flakes contribute significantly to this issue.

To address this, we present an improved method of polymer-free deterministic transfer using custom-fabricated inorganic silicon nitride cantilevers. These enable a transfer process that is also compatible with high-temperatures and ultra-clean UHV conditions.

More broadly, I will discuss working with 2D materials in a cleanroom context. This will include common fabrication strategies and historical development of techniques for working with 2D materials since the discovery of graphene in 2004 that will be of use to those integrating them into fabrication workflows.

Figure 1. UHV System located in the NGI cleanroom.

Towards functional, atomically controlled 2D systems: from molecular networks to 2D materials

Dr Adelina Ilie

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I will discuss several 2D systems where specific functionality is sought through atomic/nanoscale probing and design. In one example, I will introduce low-symmetry, chiral hydrogen- and halogen-assisted molecular networks formed through the assembly of borazatruxene molecular precursors and discuss how such networks can be modified to yield anisotropic transport and spin polarised bands. In a second example, I will show how anisotropic transport in low-symmetry transition metal dichalcogenides (TMDs), such as ReS2, can be enhanced through nanoscale structural features. Finally, I will show tailoring of electronic properties of high-symmetry TMDs, such as WSe2, through atomic scale interfaces and defects. These systems are primarily probed with scanning probe microscopy (SPM) techniques, including atomically-resolved imaging, spectroscopy, quasi-particle interference, and angle-dependent two-probe conductance, with a perspective of revealing atomic/nanoscale phenomena that impact their macroscopic behaviour. To gain further insight, these SPM techniques are complemented by other surface-sensitive techniques, such as angle-resolved photoemission spectroscopy (ARPES), and/or ab initio simulations.

Visualising Surface State in a candidate Topological Superconductor

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The interplay of superconductivity and topology stands at the frontier of moden quantum matter physics. Intrinsic topological superconductivity is important because its electronic properties are protected by the superconducting energy gap and are robust against local perturbations. Although topological superconductivity appears probable in UTe_2, its superconductive order parameter Δ_k has not yet been established. If spin-triplet, it should have odd parity so that $\Delta_{-k} = -\Delta_k$ and, in addition, may break time-reversal symmetry. A distinctive identifier of such nodal spin-triplet superconductors is the appearance of an Andreev bound state (ABS) on surfaces parallel to a nodal axis, in the form of a topological surface band (TSB). Moreover, theory shows that specific TSB characteristics observable in tunneling to an *s*-wave superconductor distinguish between chiral and non-chiral Δ_k. To search for such phenomena in UTe_2, we employ *s*-wave superconductive scan-tip imaging [1] and discover a distinct TSB signature, an intense zero-energy Andreev conductance maximum at the (0-11) crystal termination. Its imaging yields quasiparticle scattering interference evidence for two Δ_k nodes aligned with the crystal *a*-axis. Most critically, development of the zero-energy Andreev conductance peak into two finite-energy particle-hole symmetric conductance maxima as the tunnel barrier is reduced, signifies that UTe_2 superconductivity is non-chiral. Overall, this combination of a zero-energy Andreev conductance maximum at the UTe_2 (0-11) surface, internodal scattering along the *a*-axis, and splitting of Andreev conductance maximum due to *s*-wave proximity, categorizes the superconductive Δ_k of UTe_2 as the odd-parity non-chiral topological state [2].

[1] Gu, Carroll, **Wang** et al., *Nature* **618**, 921 (2023).
[2] Gu, **Wang**, Carroll et al., *Science,* in press (2024).

Altermagnetic domains imaged and controlled down to the nanoscale

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A new class of magnetic materials have recently been discovered that not only challenge our fundamental understanding of magnetism, but also show promise for technological applications from spintronics through to neuromorphics and superconductivity. These materials have been dubbed altermagnets and they combine favourable properties of both ferromagnets and conventional antiferromagnets. In this talk I will be discussing the magnetic domain imaging and manipulation of the altermagnet MnTe using both XMLD and XMCD PEEM.

Interfacial Chemistry in the Electrocatalytic Hydrogenation of CO_2 over C-Supported Cu-Based Systems

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The direct electrocatalytic hydrogenation of CO_2 using renewable energy is a key technology for defossilising and electrifying the chemical industry and producing sustainable carbon-based fuels. Consequently, this reaction is under extensive investigation. Copper (Cu) is a component of many electrocatalysts for the CO_2 reduction reaction (CO_2RR) due to its higher efficiency and selectivity towards CO_2 reduction products compared to the parasitic hydrogen evolution reaction (HER). However, current electrocatalyst performances, in terms of activity and stability, are insufficient for commercial development, necessitating the design of superior electrocatalysts.

Understanding the molecular foundations of catalytic reactions aids in designing improved catalytic materials. This contribution focuses on understanding the dynamics at the reactive Cu interface using in situ and operando methods. I will present recent advancements in characterizing the CO_2 reduction reaction (CO_2RR) and our current understanding of its mechanism based on these methods.[1-2] The primary focus will be on soft X-ray spectroscopic techniques, specifically X-ray photoelectron and absorption spectroscopies. [1-5] These techniques are unique in catalytic science as they allow monitoring the evolution of the electronic structure of light elements (C, O, N) and metallic elements simultaneously, providing information on the nature of the metal in the electrode and the chemical speciation of adsorbates and components across the reactive interface. Additionally, I will discuss recent results from our group on capturing morphological dynamics of Cu nanoparticles using in situ electron microscopy.

[1] J.-J. Velasco-Vélez, T. Jones, D. Gao, E. Carbonio, R. Arrigo, C.-J. Hsu, Y.-C. Huang, C.-L. Dong, J.-M. Chen, J.-F. Lee, P. Strasser, B. Roldan Cuenya, R. Schlögl, A. Knop-Gericke, C.-H. Chuang, The Role of the Copper Oxidation State in the Electrocatalytic Reduction of CO_2 into Valuable Hydrocarbons, *ACS Sustainable Chem. Eng.*, 7 (2019), 1485–1492.
[2] J.-J. Velasco-Vélez, C.-H. Chuang, D. Gao, Q. Zhu, D. Ivanov, H. S. Jeon, R. Arrigo, R. V. Mom, E. Stotz, H.-L. Wu, T. E. Jones, B. Roldan Cuenya, A. Knop-Gericke, R. Schlögl, On the activity/selectivity and phase stability of thermally grown copper oxides during the electrocatalytic reduction of CO_2, *ACS Catalysis*, 10 (2020) 11510-11518.
[3] J-J. Velasco-Velez, R.V. Mom, L.-E. Sandoval-Diaz, L. J. Falling, C.-H. Chuang, D. Gao, T. E. Jones, Q. Zhu, R. Arrigo, B. Roldan Cuenya, A. Knop-Gericke, T. Lunkenbein, R. Schlögl, Revealing the Active Phase of Copper during the Electroreduction of CO_2 in Aqueous Electrolyte by Correlating In Situ X-ray Spectroscopy and In Situ Electron Microscopy, *ACS Energy Lett.*, 5 (2020), 2106–2111.
[4] R. Arrigo, R. Blume, A. Large, J.-J. Velesco-Velez, M., Haevecker, A. Knop-Gericke, G. Held, Dynamics over a Cu-graphite electrode during the gas-phase CO_2 reduction investigated by APXPS, *Faraday Discuss.,* 236 (2022) 126-140.
[5] D. Gianolio, M.D. Higham, M.G. Quesne, M. Aramini, R. Xu, A.I. Large, G. Held, J.-J. Velasco-Vélez, M. Haevecker, A. Knop-Gericke, C. Genovese, C. Ampelli, M. Erwin Schuster, S. Perathoner, G. Centi, C. R. A. Catlow, R. Arrigo, Interfacial Chemistry in the Electrocatalytic Hydrogenation of CO2 over C-Supported Cu-Based Systems, *ACS Catal.*, 13 (2023) 5876–5895.

Poster Presentations

Characterising nitrogen defects in graphene grown by bottom-up synthesis

Liv Warwick[1,2], Matthew A. Stoodley[2,3], Jonathan Bradford[1], Matthew Edmondson[1], Benedikt P. Klein[2,3], Fulden Eratam[2], Henry P. Hoddinott[2,5], Luke A. Rochford[4], Reinhard J. Maurer[3], David A. Duncan[2], Alex Saywell[1]

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Recently, we have pioneered a new method for the growth of defective graphene, e.g. graphitic material containing heteroatoms or vacancies, [1] by 'bottom-up' on-surface growth methodologies. In our chemical vapour deposition process [2] we use an aromatic precursor that contains the same structural element as our desired defects. Here, using a similar method, we will present a low temperature scanning tunnelling microscopy (LT-STM), X-ray photoelectron spectroscopy (XPS) and normal incidence X-ray standing waves (NIXSW) study of graphene containing nitrogen defects, grown from a nitrogen containing precursor. By transferring the samples between the different technique chambers via an ultra-high vacuum suitcase, we were able to correlate spectroscopic differences to morphological changes on the surface.

[1] Bhatt, M. D. et al. RSC Adv. 12, 21520-21547 (2022) [2] B. P. Klein. et al. Appl. Phys. Lett., 2022, 121, 191603.

Structural details of conjugated polymers uncovered by ESD-STM

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Conjugated polymers (CPs), within organic semiconductors have attracted significant attention, due to their remarkable conductivity, mechanical flexibility, and cost-effective processability. These attributes position CPs as highly promising candidates for a broad variety of applications, including optoelectronics, thermoelectrics, sensors and bioelectronic devices.

The innovative combination of electrospray deposition (ESD) with scanning tunnelling microscopy (STM) in an ultrahigh vacuum environment, a recent advancement from the Costantini Group, offers an unprecedented opportunity to gain detailed, molecular-scale insights into the structure, conformation, and assembly of surface-adsorbed conjugated polymers. This level of analysis remains unattainable by any other existing analytical technique. The electrospray ionisation process enables the controlled and intact soft-landing of sub-monolayer coverages of CPs onto atomically clean and flat single crystal surfaces, while preserving the CP original sequence and structure. The resulting surfaces are analysed by high-resolution STM, which provides direct evidence about the preferential assembly configurations of CPs, their stacking distances, the polymer mass distributions, the exact backbone sequences and the side chain conformations.

Here, I present three case studies, each focusing on a different aspect: the analysis of polymerization defects in pBTTT-OR-R, the determination of the mass distribution in pgBTTT, and the determination of the assembly and backbone conformation of p(NDI2OD-T2).

This in-depth structural analysis, which surpasses the capabilities of standard analytical techniques in polymer science, provides quantitative information essential for establishing a reliable structure-function relationship of these materials.
ESD-STM, therefore, sets the stage for the development of novel, more environmentally friendly, and enhanced synthetic polymerization strategies for this important class of functional materials.

From molecules to metal doped graphene

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Doping graphene with transition metals has been predicted to lead to promising electronic, (electro-)catalytic and gas sensing properties.[1][2] We have investigated the synthesis of transition metal doped graphene using a molecular precursor, Fe-tetraphenyl porphyrin chloride (Fe- TPP). The central ion, Fe2+, is desirably retained in the graphene structure under growth conditions. The chosen substrate, Ni(111), is known to promote graphene formation at low temperature (400 °C).[3] We have investigated the molecular deposition and graphene formation by means of UPS, XPS and STM techniques, optimizing the process of graphene formation and functionalization. The common pathway for graphene on Ni includes heating around 600 °C in presence of a hydrocarbon gas. We avoided this route since it involves dissolution of carbon in the bulk. We found that a polymerization approach allows to operate at lower temperatures which is beneficial for the preservation of the Fe loading. More specifically, we have deposited a molecular overlayer holding the sample between 250 °C and 350 °C and keeping it at such temperature for several hours. Our data reveals a change in the oxidation state of the central metal ion. Indeed, from the starting oxidation number (in powder state Fe3+) iron is reduced to Fe2+ on the sample, with no detectable signal of Cl-. A combined STM investigation elucidated the surface geometry, including the iron-induced defects, revealing one-dimentional linear structures.
In conclusion, we have found a novel promising route to incorporate transition metals into the graphene mesh that may lead to relevant applications.

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[1]J. Ni et al., Phys. E: Low-Dimens 116(2020)113768
[2]Y. Wang et al., ACS Catal. 2022,12,9,407–5415
[3]C.-M. Seah et al., CARBON 70(2014)1–21

Boosting Thermoelectric Performance of Self-Assembled Monolayers Using Molecular Templating

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The observation of room temperature quantum interference (QI) effects in single molecules has opened up new possibilities for molecular electronics and thermoelectric materials. Molecular junctions are generally modelled and simulated using idealised contacts between the molecule and electrodes, something which does not translate easily to experiment when dealing with molecular films. Despite this, several recent reports now demonstrate that single-molecule QI effects can be translated into self-assembled monolayers (SAMs) [1 2], which retain excellent thermoelectric properties, even with the absence of long-range order within the layers. The common wisdom is that to improve on this, the surface quality must be improved such that molecular ordering and the consistency of surface-molecule contacts must be improved.

Previously, a multi-component self-assembly structure consisting of an OPE3 structure around an anthracene core (Figure 1a) combined with a layer of zinc-tetraphenylporphyrin (Zn-TPP) on top has been shown to give a 50% to 100% improvement in the Seebeck coefficient [3]. Here, we reverse the structure using a combination of vacuum deposition and self-assembly on the same surface to create a layer of zinc-phthalocyanine (ZnPc) (Figure 1b) on an Au(111) surface and self-assemble the anthracene OPE3 on top. This gives the Seebeck benefit previously demonstrated whilst also providing a template layer for the anthracene OPE3. The pyridine anchor groups bind to the zinc cores which should improve the long-range molecular ordering of the SAM.

The anthracene OPE3 is dissolved in chloroform and can produce a SAM of height associated with the molecules standing up (Figure 1c). The ZnPc layer can withstand being placed in chloroform for the deposition time without compromise to the monolayer structure (Figure 1d). A sample can therefore be produced combining the two techniques to create the desired multilayer structure.

Temperature programmed bottom-up surface polymerisation of graphene nanoribbons

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Over the past few decades, the size of electronics has been rapidly decreasing leading to major advancements in molecular electronics, in which the ultimate goal is to create single molecule electronic components [1]. One dimensional structures such as graphene nanoribbons (GNRs) [2] have become especially promising, partly due to their exceptional conductance and potential for high on-off ratios when integrated into electronic components [3,4]. The challenge remains that even small defects in the edges of these molecular wires can cause scattering and localisation of electrons, making bottom-up fabrication via on-surface synthesis an ideal method for defect free GNR growth [5].

Here, we use the precursor monomer 10,10'-dibromo-9,9'-bianthryl (DBBA) to fabricate GNRs on atomically flat Au(111) surfaces. DBBA is deposited under ultrahigh vacuum (UHV) conditions and subsequently annealed to thermally induce polymerisation and cyclodehydrogenation, forming molecular wires with a width of 7 carbon atoms. GNR growth is characterised in situ using temperature-programmed X-ray photoelectron spectroscopy (TP-XPS) and studied in ambient conditions using molecular-resolution atomic force microscopy (AFM) (see Figure 1 for a) images and b) description of the growth process). Following this, we discuss how to apply ambient high-resolution AFM to study on-surface growth on insulating surfaces, where polymerisation is catalysed by extrinsic metal cluster catalysts.

Molecular materials for carbon capture and storage: On-surface characterisation of self-assembly and thermal stability of metal phthalocyanines

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The successful capture and storage of carbon- and nitrogen - containing greenhouse gases (e.g. CO2 and NOx - produced by industrial processes) is of significant environmental importance; materials enabling gas sequestration are a route to reducing the effects of climate change. Molecular based materials, containing units which can ligate and trap gas molecules, may provide a way of selectivity and efficiency removing pollutants. Porphyrins and phthalocyanines (Pcs), both of which can be functionalised with reactive metal atoms, have been extensively studied in ultra-high vacuum (UHV) conditions.[1] Importantly, the ligation of gaseous species to the metal centres of such molecules has been shown to be feasible. [2] Here we study the formation of molecular arrays of iron phthalocyanine (FePc) on Au(111) under systematically controlled thermal conditions. We employ UHV scanning tunnelling microscopy (UHV-STM) and X-ray photoelectron spectroscopy (XPS) to characterise the morphology and chemistry of the on-surface synthesised structures and investigate thermal stability of the Pc macrocycle and extended molecular islands.

[1] J. M. Gottfried, Surf. Sci. Rep. 70, 259 (2015)
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Visualising the steps in a chemical reaction: On-surface reactivity of brominated tetraphenyl porphyrin on Cu(111)

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Scanning probe microscopy techniques have been extensively employed to provide details of on-surface reactions [1] and can provide significant insight into the effects of substrate and molecular chemistry upon the reaction products of on-surface synthesis.[2] The Ullmann-type coupling of brominated tetraphenyl porphyrin (BrxTPP) on Au(111) [3] is a seminal work, demonstrating molecular characterisation of on-surface covalent coupling. However, on Cu(111) the reaction progress is different,[4] and for various substrates a variety of reactions (including; ring-closing, metalorganic coordination, and self-metalation) may occur. Here, we detail a low-temperature ultra-high vacuum scanning tunnelling microscopy (STM) study of BrxTPP (x=0-4) on Cu(111). We observe multiple steps in an on-surface reaction; debromination, formation of metal-organic frameworks, ring opening, self-metalation, and covalent coupling. Systematic, temperature controlled, investigation reveals step-wise evolution of the reaction, with the intermediate reaction stages probed using STM imaging and manipulation.

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[4] C.M. Doyle et. al, Chem. Commun. Camb., 2011, 28, 12134