Symposium on “Charge Transfer in Metal-Organic Systems at Surfaces”

University of Warwick, Institute of Advanced Study

Wednesday, November 14, 2018

Meeting location: Scarman Conference Centre (click for directions)

Metal-organic complexes, assemblies, and networks at surfaces are of growing interest due to the vast library of two dimensional architectures that have been discovered and the interest in applying these systems toward novel chemical and electronic applications. As this field matures, important fundamental questions remain as to the electronic, charge transfer, and redox character of the components of these systems, as these issues are at the centre of their most interesting properties.

This symposium is supported by the Institute of Advanced Study and the Materials Global Research Priority (GRP) at the University of Warwick, as well as the Royal Society of Chemistry and the Institute of Physics.
Symposium Program – Wednesday, November 14

10:00  Welcome by Prof. Giovanni Costantini, University of Warwick

10:10  Prof. Hans-Peter Steinrück, Friedrich-Alexander-Universität, Erlangen-Nürnberg
       “In Situ Metalation of Porphyrins on Metal and Oxide Surfaces”

10:55  Prof. José Ignacio Pascual, CIC nanoGUNE, Donostia San Sebastián
       “Charge redistribution & spin localization in molecular systems on surfaces”

11:40  Discussion

12:00  Lunch and Posters

13:30  Prof. Steven Tait, Indiana University
       “Metal-ligand Redox Assembly at Surfaces for Single-site Catalysts”

14:15  Prof. Reinhard Maurer, University of Warwick
       “A First-Principles Perspective on the Electronic and Spectroscopic Signatures of
       Charge Transfer at Metal-Organic Interfaces”

15:00  Discussion

15:20  Poster and Coffee Break

15:50  Prof. James O’Shea, University of Nottingham
       “Resonant core-level spectroscopies for probing the electronic structure and charge
       transfer dynamics of molecules at surfaces”

16:35  Prof. Nian Lin, Hong Kong University of Science and Technology
       “Charge Transfer in Metal-Organic Systems: from Local Contacts to Delocalized Bands”

17:20  Discussion

17:40  Concluding Remarks by Prof. Costantini

Location

Scarman Conference Centre
University of Warwick
Directions to the Scarman Centre: https://warwick.ac.uk/services/conferences/location/
Google maps: https://goo.gl/maps/N6VfSKJvqPt

For information about reaching the University of Warwick by bus, train, or car (also info about
visitor parking), see: https://warwick.ac.uk/about/visiting/
In Situ Metalation of Porphyrins on Metal and Oxide Surfaces

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Metallotetrapyrrole complexes are versatile functional building blocks in many biological and biochemical processes. In addition, these molecules are also 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 in particular the synthesis of metalloporphyrin monolayers by direct metalation of free base porphyrins, under UHV conditions and in the liquid phase.

References:

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Metallic surfaces supporting molecular systems behave not only as source/drain of charge, but also may catalyze reactions, rehybridize bonds, screen electron charges, or facilitate strong redistributions of electrons. In some cases, the combination of various of these surface-induced effects may end up in the stabilization of paramagnetic molecular states.

In this seminar I will present several paradigmatic cases of charge redistribution in molecular systems on surfaces resolved with scanning tunneling microscopy and spectroscopy. I will start with a prototypical charge-transfer system, TTF-TCNQ, which on the Au(111) surface recovers an integer charge localization on the electron acceptor species, resulting in a spin-polarized system [1,2]. Charge redistribution can also be enabled through the incorporation of specific electron acceptor or donor groups. I will analyze results on CN and NH2 functionalization of the edges graphene nanoribbons [3]. The role of the surface will also be presented though a model experiment, picturing the change of valence state of a metal porphyrin as it is detached from the surface. Finally, I will show a case example of electron redistribution in a conjugated graphene nanostructure, resulting in spin localization at specific edge sites [4].

References:
1. *Vibrational Kondo effect in pure organic charge-transfer assemblies*  
2. *Gating the charge state of single molecules by local electric fields*,  
3. *Doping of Graphene Nanoribbons via Functional Group Edge Modification*  
4. *Single Spin Localization and Manipulation in Graphene Open-Shell Nanostructures*  

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A grand challenge in heterogeneous catalysis is to achieve high levels of selectivity by controlling the chemical uniformity of metal catalyst sites at surfaces. There is currently a significant effort, using a variety of strategies, to achieve well-defined and stable single-site transition metal centers at surfaces. Our group is working to apply principles of on-surface metal-organic complexation to develop a new approach. Metal-organic coordination networks at surfaces, formed by on-surface redox assembly, can provide specific and selective chemical function, but there is a limited understanding of the chemical reactivity of these systems. We tested chemical activity of vanadium single-site complexes that are stabilized by tetrazine-based ligands [1]. We demonstrate activity toward dioxygen activation and a high degree of selectivity compared to vanadium nanoparticles. Reaction with O$_2$ causes an increase in V oxidation state from V$^{IV}$ to V$^{VI}$, resulting in a single strongly bonded V-oxo product and spillover of O to the Au surface. This demonstrates the high chemical selectivity of single-site metal centers in metal-ligand complexes at surfaces compared to metal nanoislands. The metal centers are stabilized in extended, ordered metal-organic complexes that self-assemble through an on-surface redox process on the Au(100) surface and are characterized by X-ray photoelectron spectroscopy, scanning tunneling microscopy, high-resolution electron energy loss spectroscopy, and density functional theory. The theoretical work and novel synthesis involved in this project rely on close collaboration in our interdisciplinary team. We are working to extend these chemical studies to more complex systems that include earth abundant metals and other ligand designs, which will also be highlighted in this presentation.

We have also developed synthesis schemes to assemble these quasi-square planar metal-organic complexes on high surface area powdered oxides through a modified wet-impregnation-style method [2]. X-ray photoelectron spectroscopy measurements demonstrate loading of metal and ligand on the surface and synchrotron-based X-ray absorption spectroscopy measurements of the coordination shell of the metal centers demonstrates single site formation rather than nanoparticle assembly. These systems are shown to be active for the catalysis of hydrosilylation reactions at a level that is competitive with current homogeneous catalysts.


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A First-Principles Perspective on the Electronic and Spectroscopic Signatures of Charge Transfer at Metal-Organic Interfaces

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A fundamental understanding of molecular structure and chemical reactivity at complex metal-organic interfaces is key to many technological applications ranging from molecular electronics to functionalized surfaces and light- and electron-enhanced heterogeneous catalysis. Predictive ab-initio electronic structure methods based on Density Functional Theory enable to gain such an understanding through an accurate computational description of interface structure, spectroscopy, and reactivity, (1) all of which intimately depend on the nature and magnitude of molecule-metal charge-transfer. On prototypical example systems such as the photo-induced isomerization of metal-adsorbed azobenzene molecules (2, 3) and porphyrine-based thin-films,(4, 5) I will explain the computational techniques and methodological underpinnings that give rise to a robust computational characterization of interfaces. A focus herein will be on the connection of measurable properties, such as quantitative structural measurements and surface core-level spectroscopic signatures to the charge localized on an adsorbed molecule – a quantity that is unfortunately not uniquely defined. (6)


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Resonant core-level spectroscopies for probing the electronic structure and charge transfer dynamics of molecules at surfaces

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In devices such as dye-sensitised solar cells, the dynamics of charge transfer at the electron injection interface – from the molecule into the semiconductor substrate – play a key role and are typically very fast. The charge transfer dynamics of the molecule biisonicotinic acid adsorbed on a titanium dioxide surface was found to occur on the low femtosecond timescale – using a core-hole clock implementation of resonant photoemission (RPES). This process relies on the competing channels of core-hole decay and ultra-fast charge transfer to the surface. An electron emitted by a core-hole decay process in which the originally excited core-electron is a direct participant and is easily identified within the electronic debris by its kinetic energy and evinces electron localization in the excited molecular orbital on the timescale of the core-hole lifetime. It has long been proposed that the photons emitted during radiative core-hole decay should be equally informative, allowing femtosecond charge transfer to be probed in more realistic environments due to the large escape depth of the photons in what would be resonant inelastic x-ray scattering (RIXS) compared to the electrons of resonant photoemission (RPES). In the event that the originally excited core-electron is a direct participant in the decay process, radiative decay will give rise to what is essentially an elastically scattered soft x-ray photon, perhaps modified by any ultra-fast processes within the core-excited molecule. Moreover, the other photons emitted in the experiment – the inelastic scattering – provide valuable insight character of the occupied molecular orbitals and their relationship to each other. This is most evident when the RIXS is mapped over all the highest occupied molecular orbitals as a function of core-excitation into all the lowest unoccupied molecular orbitals.

In this talk I’ll discuss RPES and RIXS maps of biisonicotinic acid molecules in the crystalline phase, multilayer film and the adsorbed monolayer on TiO2(110) and show how these two complementary techniques reveal the ultra-fast charge transfer dynamics across the interface and also ultra-fast vibronic coupling within the molecules themselves.

References

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Charge Transfer in Metal-Organic Systems: from Local Contacts to Delocalized Bands

Nian Lin
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Using low-temperature scanning tunneling microscopy and spectroscopy, we investigate atomic contacts between metal atoms and organic molecules. I will discuss how the molecular orbitals are modified by the single and multiple atomic contacts. I will also present our recent efforts of synthesizing pi-conjugated metal-organic systems that show dispersive band structures. These systems are anticipated to exhibit interesting electronic properties, such as metallicity, superconductivity or anomalous quantum Hall effects.

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An investigation of double molecular layers of C\textsubscript{60}/C\textsubscript{70} and C\textsubscript{70}/C\textsubscript{70}

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As the simplest fullerene molecules, research related to structural and electronic properties of C\textsubscript{60} and C\textsubscript{70} investigated. [1] They are two typical model molecules for the investigation of molecular self-assembly on surfaces. Both molecules, when deposited onto a solid substrate, have the tendency to form close-packed molecular layers. Because of the similarity between C\textsubscript{60} and C\textsubscript{70}, there is an interest in exploring the possibility of making a molecular “alloy”. The different geometric shapes of the two molecules, however, seem to prevent a regular structured molecular alloy to form. [2] In addition to the idea of a molecular alloy, it is also interesting to see if a fullerene crystal can be formed with alternating layers of C\textsubscript{60} and C\textsubscript{70}.

We have conducted experiments to study how a layer of C\textsubscript{60} interacts with a layer of C\textsubscript{70}. The first layer C\textsubscript{70}/C\textsubscript{60} is deposited on Au(111) substrate at room temperature in ultra-high vacuum. Then a partial second layer of C\textsubscript{60}/C\textsubscript{70} was added. We image the molecular layers using an Omicron VT-STM. Images are acquired after the sample has been annealed to successively higher temperatures, allowing the identification of any exchange of molecules between the layers.


POSTER PRESENTATION

**High intensity electrospray source for UHV deposition of large functional molecules for in-situ STM studies**

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Electrospray ionisation beam deposition (ESI-BD) is quickly becoming a versatile technique for depositing large thermally labile molecules for study on surfaces in vacuum. The technique has been used to demonstrate deposition and study of a wide range of molecules such as molecular magnets, biomolecules, and porphyrin nanorings. A new ESI-BD instrument will be presented, which has been designed for high efficiency and high transmission, coupled with a variable temperature Scanning Tunnelling Microscope (STM), that offers the ability to study complex systems with the ultimate spatial resolution. Molecules are delivered from solution in atmospheric conditions to a sample surface located in ultrahigh vacuum (UHV), by electrospray ionisation, followed by several ion optic elements that guide and mass-select ions through successive differential pumping chambers with high transmission. By adjusting deposition voltage it is also possible to adjust the molecule impact energy, from the soft landing to the ballistic impact regime. STM images and analysis of a selection of large molecules will be presented, demonstrating the capabilities of this scientific instrument for nanoscale molecular visualisation.
Bottom-up self-assemblies of organic molecules offer a realistic solution toward the fabrication of next-generation functional materials and devices. In this work, we present a focused investigation on the assembly of a porphyrin, i.e. the zinc-tetraphenylporphyrin (ZnTPP), on the Au(111) surface. A combined analysis of scanning tunneling microscopy imaging and X-ray photoemission spectroscopy measurements allows to gain essential information concerning the molecular packing as well as the molecules-substrate interaction. At odd with previous results, a noteworthy interaction between the monolayer of the ZnTPP molecular self-assembly and the metal surface is observed, confirming the formation of a metal-organic interface. Furthermore, we report, for the first time, molecular diffusion effects of the second layer pointing out a weak interaction between the deposited molecular layers.
Since the conception of scanning tunnelling microscopy (STM) in 1981, many other scanning probe microscopy (SPM) techniques have been developed, including in the field of electrochemistry, where scanning electrochemical microscopy (SECM) has found many applications. While scanning electrochemical probe microscopes are powerful tools for the spatial mapping of electrochemical reactivity (e.g., electrocatalytic activity) at the micro- to nanoscale, they are often limited in their ability to reliably map topography. Herein, a combined STM-SECM technique is proposed for simultaneous high resolution topographical and electrochemical imaging (mapping). The challenge of bridging the differing length scales of the two individual techniques (i.e., nano- to Angstrom-scale for STM versus micro to nanoscale for SECM) has been addressed using a “hopping mode” regime, thereby allowing for the study of features that are larger than are normally observable in STM whilst still being able to map smaller features. Significant progress has been made in the fabrication of robust and reproducible STM-SECM probes, manufactured from laser-pulled quartz capillaries filled with pyrolytic carbon, on which electrocatalytically active metals (e.g., Pt) can be electro-deposited, resulting in well-defined and stable probe tips. Herein, these probes have been used to carry out joint STM-SECM studies on sample systems to correlate topography and electrocatalytic activity at the nanoscale, using \{111\}-oriented two-dimensional Au nanocrystals, AuNCs, as an exemplar system (e.g., see Fig. 1).

Fig 1. SEM, STM and SECM (left to right) images of a single AuNC. The STM (topography) and SECM (electrochemical activity) maps were obtained synchronously using a “hopping pulse mode” of STM-SECM in 0.1 M HClO4. SECM was operated in the substrate generation/tip collection mode, detecting the product (H2) of the hydrogen evolution reaction at the substrate.

Halogen bonding interactions have recently emerged as a powerful driving force for the self-assembly of surface-confined monolayers\textsuperscript{1,2}. One potential application of halogen bonds is as a cooperative interaction paired with hydrogen bonds. The simultaneous use of these two strong, directional interactions may offer additional levels of control over the self-assembly process. In this work, we demonstrate that hydrogen and halogen bonds are able to cooperatively drive the self-assembly of complex networks at the solid-liquid interface. Pairing a molecule which can act as both a hydrogen and halogen bond donor with a molecule which can act as an acceptor for both interactions results in a series of bimolecular networks. Interactions including Br···N(pyridyl) and Br···O halogen bonds, in addition to O-H···N(pyridyl) hydrogen bonds are all shown to be significant.
