

Gaining Mechanistic Insight in Heterogeneous Catalysis at the Single Molecule Level: Orbital Imaging of a Macromolecular Catalyst and Intermediates by Scanning Tunnelling Microscopy

Sarah A. Burke, Department of Physics & Astronomy, Department of Chemistry, and Stewart Blusson Quantum Matter Institute, University of British Columbia, Vancouver, Canada V6T 1Z4

Following the first capability-building year of this project and several major repairs to the core infrastructure required in the early part of this second year, progress towards the goals of the funded ACS PRF project has been rapid. Three publications (described below) pertaining to the terpyridine-based ligand and nascent catalyst have appeared in excellent journals, and rapid progress exploring the reactivity of the surface-anchored Fe(tpy) catalyst using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS) and atomic force microscopy (AFM) has been made.

Characterization of the nascent surface-bound Fe(tpy)-based catalyst

Three publications are now in print that describe aspects of the ligand interaction with the surface and the self-assembly, structure, and electronic structure of Fe(tpy) complexes and linear chains. The first describes the selective hybridization of the tpy group of the bisterpyridine biphenyl (TPPT) molecule with the Ag(111) substrate. While other orbitals remain relatively unperturbed, the tpy-associated LUMO+1 strongly hybridizes with the noble metal surface, broadening the state significantly. This has two consequences: on the one hand the functional group one hopes to exploit is significantly changed upon adsorption on the surface, however, this also opens up the possibility of tuning interfacial electronic states through molecular functionalization. This article titled “Selective Hybridization of a Terpyridine-Based Molecule with a Noble Metal” appearing in JPCC was co-authored by 5 former trainees, two of which were partially funded by this ACS PRF grant. [1] Following on this work, the self-assembly of Fe(tpy) structure via addition of Fe atoms at various temperatures and annealing conditions gave us insight in to the self-assembly process. Isolated Fe-TPPT complexes are found with one or two Fe sites, while these complexes can also form linear chains of >10 molecular units linked by what appear to be linear tri-iron nodes. The electronic structure of both the isolated Fe-TPPT complexes and chains is explored to examine the frontier orbitals likely involved in reactivity showing an occupied Fe state just below ($\sim -0.1\text{eV}$) the Fermi energy and ligand-centered LUMO above ($+1.5\text{eV}$) the Fermi energy. This work appeared in ACS Nano earlier this year as “Designing Optoelectronic Properties by On-Surface Synthesis: Formation and Electronic Structure of an Iron–Terpyridine Macromolecular Complex” and was co-authored by 6 former trainees, two of which were partially funded by this ACS PRF grant. [2] Further work led by my former postdoctoral researcher Dr. Schiffrin used further STM data, along with AFM, XPS, XAFS, and additional modelling provided strong evidence of the tri-iron node proposed and a positive charge state on the Fe atoms attached to the tpy moiety. This work included data acquired by my former trainee Dr. M. Capsoni, who participated in the XPS and XAFS experiments at the Australian Synchrotron supported by this ACS PRF grant. This work, titled “Iron-based trinuclear metal-organic nanostructures on a surface with local charge accumulation” appeared in Nature Communications earlier this year. [3]

To continue with the planned reactivity experiments, the ligand was switched to a single phenyl linkage between the two terpyridine (TPT). This resulted in a lower proportion of chain formation, but more isolated coordinatively unsaturated Fe-TPT complexes. The electronic structure of the Fe-TPT nascent catalyst is nearly identical to the Fe-TPPT catalyst with a Fe-centered HOMO slightly closer to the Fermi energy ($\sim -0.07\text{eV}$) and more localized LUMO (due to the single phenyl rather than bi-phenyl). This

trend is consistent with previous work. This work, and the following work on reactivity of the Fe-TPT complexes constitutes the MSc thesis work of M. DeJong (expected Dec 2018).

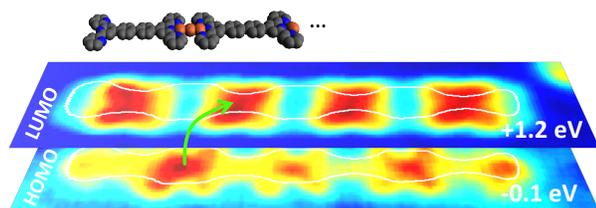


Figure 1: Electronic density of states (from STS maps) of the metal-centered HOMO and ligand-centered LUMO of Fe-TPPT chains

Reactivity of the Fe(tpy) catalyst towards small molecules

Using the capability built up during the first year of the ACS PRF grant to expose our prepared surface-bound catalyst to gaseous reactants, we have made significant progress on exploring the reactivity of our isolated Fe-TPT catalyst towards CO and ethylene. As CO is always present to some level in UHV, and is required for submolecularly resolved imaging by tip-functionalized nc-AFM, we deliberately dosed CO on the surface to explore the reactivity towards this already present species. A bound CO complex similar to that seen for Fe-TPPT in [3] is identified, however in our work we see two distinct CO-bound complexes. Following dosing of ethylene, additional new species appear. STS measurements show shift of the Fe state away from the Fermi energy following small molecule attachment indicative of a chemical reaction, with different shifts appearing for CO and ethylene. A total of 6 distinct species following CO and ethylene dosing and annealing have been observed. Using a combination of STM, STS, and tip-functionalized nc-AFM imaging we are currently working to identify all 6 reacted Fe-TPT species as well as the progression from one to another with annealing treatment. This work is ongoing and requires theory support that is being explored through a new collaboration.

The reactivity of the Fe-TPT chains is also being investigated, however the increased complexity of this structure, the lower density of this site on the as-prepared surface, and apparent lower reactivity have not enabled us to draw any conclusions at this time about attachment geometry or structure of CO or ethylene at these sites. This work is also ongoing, and will be the subject of studies carried out by a current MSc student and new postdoctoral researcher.

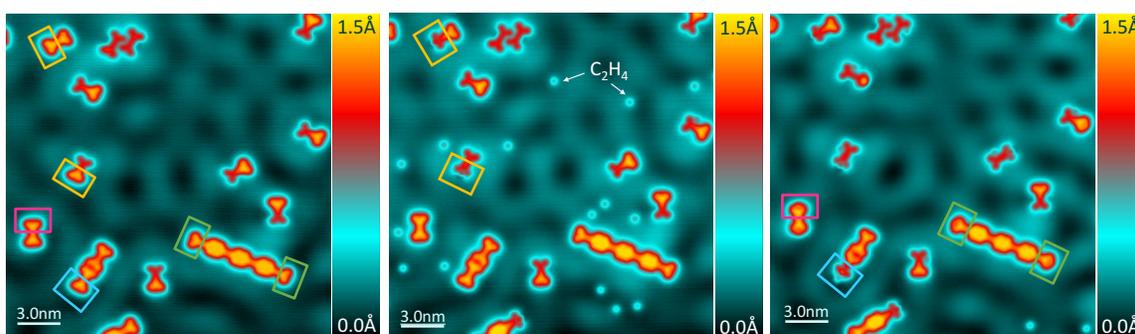


Figure 2: Progression from clean surface, dosing with CO and ethylene, and following annealing. Changes in the terminations of the Fe-TPT complexes are seen on dosing and annealing.

[1] M. Capsoni, A. Schiffrin, K. Cochrane, C.-G. Wang, T. Roussy, A. Q. Shaw, W. Ji, **S. A. Burke***, *Journal of Physical Chemistry C*, 121(42) (2017); 23574-23581

[2] Agustin Schiffrin, Martina Capsoni, Gelareh Farahi, Chen-Guang Wang, Cornelius Krull, Marina Castelli, Tanya S. Roussy, Katherine A. Cochrane, Yuefeng Yin, Nikhil Medhekar, Adam Q. Shaw, Wei Ji*, and **Sarah A. Burke***, *ACS Nano*, 12(7) (2018); 6545-6553

[3] Cornelius Krull, Marina Castelli, Prokop Hapala, Dhaneesh Kumar, Anton Tadich, Martina Capsoni, Mark T. Edmonds, Jack Hellerstedt, **Sarah A. Burke**, Pavel Jelinek and Agustin Schiffrin*, *Nature Commun*, 9 (2018); 3211