

# CHEMISTRY SEMINAR

## Determining catalytic activity of mini-metalloenzymes

By Micaylah Bowers '23 BMB

11:30 a.m.

April 6, 2023

Darrah Auditorium  
McCreary Hall Room 101

### Abstract:

Titanium, although abundant and relatively inexpensive, is rarely used by nature due to its high propensity to hydrolyze in an aqueous environment. However, mini-metalloenzymes (MMEs), which are known to stabilize hydrolysis prone metal ions by disrupting the unwanted reactivity that normally occurs, have made the use of these reactive metal ions possible. Utilizing well characterized de novo designed Due Ferri single chain (DFsc) proteins, we have successfully shown binding to hydrolysis prone metals such as  $\text{Zn}^{2+}$ ,  $\text{Ti}^{4+}$ , and  $\text{V}^{5+}$  and their reactivity, resulting in the first functional titanium metalloenzyme. Upon further modification of their active sites, we have enhanced the reactivity of these metal-bound DFsc proteins by introducing a tyrosine residue, which is known to bind particularly well to titanium. Catalytic activity of these MMEs has been monitored via DNA cleavage and small molecule colorimetric and nuclear magnetic resonance assays, which have shown that our tyrosine modified metalloenzymes have differences in reactivity based on protein sequence.

# CHEMISTRY SEMINAR

## Impact of Sample Volume and Dopant on the “Memory Effect” of Clathrate Hydrates

By Meem Noshin Nawal Khan '24 Chemistry

11:30 a.m.

April 6, 2023

Darrah Auditorium  
McCreary Hall Room 101

### Abstract:

Clathrate hydrates are a class of inclusion compounds consisting of guest molecules trapped in water cages. Based on the size and shape of guest molecules, different sizes of water cages are stabilized. Different cages are combined to form larger crystal structures, most commonly cubic sI and sII hydrates. Clathrate hydrates tend to exhibit “memory effect”, i.e., clathrates form more easily from melts of previously formed hydrates instead of from freshly mixed components. The purpose of this study is to test the memory effect in clathrate hydrates of tetrahydrofuran (THF) and to investigate what role (if any) the volume of samples and different concentrations of methanol doping has on memory effect. Fresh solutions of THF and water in the ratio of 1:17. Pure samples of different volumes were tested at 1.5 °C. None of the samples formed hydrates. Therefore, they were undercooled to -30 °C and then checked at 1.5 °C to confirm hydrate formation. These samples were then melted above the THF-hydrate melting point (> 4.2 °C) and then re-cooled to 1.5 °C to see if hydrates re-formed. The same experiment was done with solutions doped with different percentages of methanol. It was observed that for all the experiments, memory effect was seen in more samples as the volume of solution was increased. Memory effect disappeared as the volume of solution was reduced to 50 µL. It was also observed that increased concentration of methanol in solution prevented memory effect. In a given volume of samples, hindrance of memory effect became stronger with higher percentage of methanol. In a given concentration of methanol as a dopant, memory effect reduced with reduction of volume of the samples. It was also seen that memory effect almost disappears when the concentration of methanol is increased to 2%.

# CHEMISTRY SEMINAR

## Reactivity of a Trimethylamine-ligated (Cyclopentadienone)iron Carbonyl Compound

By Bryn K. Werley '23 Chemistry

11:30 a.m.

April 6, 2023

Darrah Auditorium  
McCreary Hall Room 101

### Abstract:

Valued for their ease of synthesis, sustainability, and low cost, (cyclopentadienone)iron carbonyl catalysts have important applications in redox chemistry, which has historically required stoichiometric oxidants and reductants or catalysts containing rare platinum-group metals. There is spectroscopic evidence that trimethylamine-bound (cyclopentadienone)iron carbonyl species form in solution during the activation of tricarbonyl compounds with trimethylamine *N*-oxide, but they have not previously been isolated. The synthesis, isolation, and characterization of a trimethylamine-ligated (cyclopentadienone)iron carbonyl compound and its application to transfer hydrogenations and dehydrogenations are reported.

In contrast to widely known (cyclopentadienone)iron tricarbonyl compounds, this trimethylamine-bound species requires no activation by trimethylamine *N*-oxide, base, or UV light. Characterized by X-ray crystallography and previously observed under hydrogenation and dehydrogenation conditions via NMR spectroscopy, the trimethylamine adduct is thought to form as a stabilizing, off-cycle intermediate. The catalytic activity of this novel species in transfer hydrogenations and dehydrogenations will be discussed and compared to the activity of its tricarbonyl analog. The trimethylamine-bound precatalyst was also used in kinetic isotope effect studies, which suggested hydrogen transfer as a rate-determining step in the reactivity of (cyclopentadienone)iron carbonyl compounds.

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### Scheme 1. Catalytic Cycle of (Cyclopentadienone)iron Tricarbonyl Catalysts in Transfer Hydrogenations and Transfer Dehydrogenations

