

# Development of Water Splitting Catalysts Using a Novel Molecular Evolution Approach

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PD12

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# Nature has Developed a Very Efficient Water Splitting Catalyst – How Can We Mimic this?

- Based on protein/metal interactions
- Runs near the thermodynamic limit
- Very specific

Can we develop an iterative chemical evolution method for generating a metal peptide catalyst with similar activity?

# Overview

## Timeline

- Start - July 1, 2005
- Finish - June 30, 2009
- 60% Complete

## Budget

- Total Project Funding
  - DOE - \$1,200,000
  - Contractor - \$300,000
- Funding for FY08
  - \$150,000 DOE
  - \$43,000 Contractor

## Barriers

- Barriers addressed
  - H. System Efficiency
  - J. Renewable Integration

## Partners

- CombiMatrix Corp., Mukilteo, WA
- Prof. Bill Armstrong, Boston College

## Objectives

- **Design and synthesize a peptide based electrocatalyst for water splitting using principles learned from photosystem II**
- **Optimize the function and stability of this electrocatalyst through iterative creation and analysis of libraries**
- **Efficient water splitting catalysts are required for effective electrolysis**

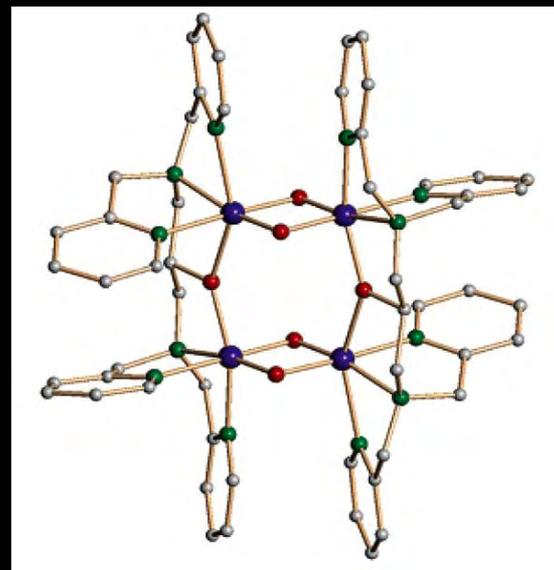
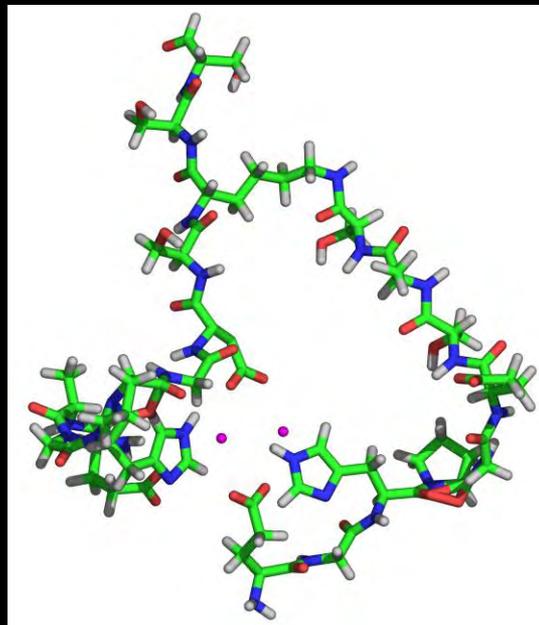
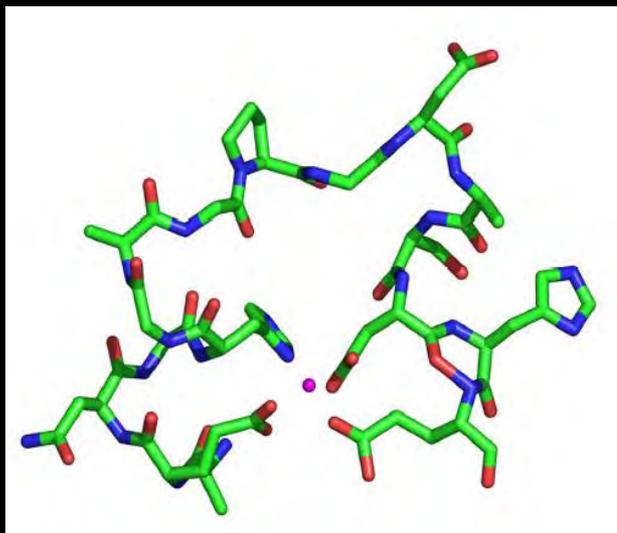
## Milestones

	Description	Completion Date	% Complete
<b>Task 1</b>	<b>Optimize light directed peptide synthesis</b>	<b>9/30/2006</b>	<b>100</b>
<b>Task 2</b>	<b>Develop electrochemically directed synthesis</b>	<b>7/30/2008</b>	<b>80</b>
<b>Task 3</b>	<b>Measure Electrochemical Baseline</b>	<b>6/30/2006</b>	<b>100</b>
<b>Task 4</b>	<b>Fabricate electrode arrays for light directed synthesis</b>	<b>6/30/2007</b>	<b>100</b>
<b>Task 5</b>	<b>Develop high throughput electrochemical analysis</b>	<b>6/30/2008</b>	<b>80</b>
<b>Task 6</b>	<b>45% Increase in catalysis over baseline</b>	<b>6/30/2009</b>	

# Approach

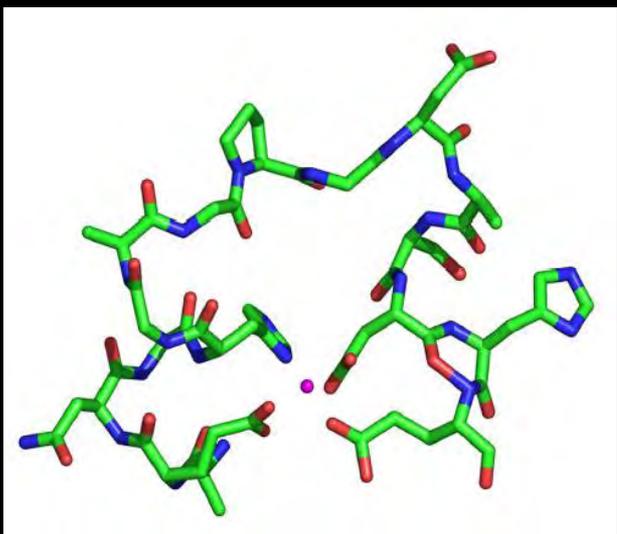
- Design and validate initial metal binding peptides
- Synthesize large arrays of peptide variants on electrodes
- Characterize the activity of each of the metal binding peptides
- Use analysis of initial array to develop a new array
- Iteratively optimize catalytic function

# RESULTS 1: Design and validate initial metal binding peptides

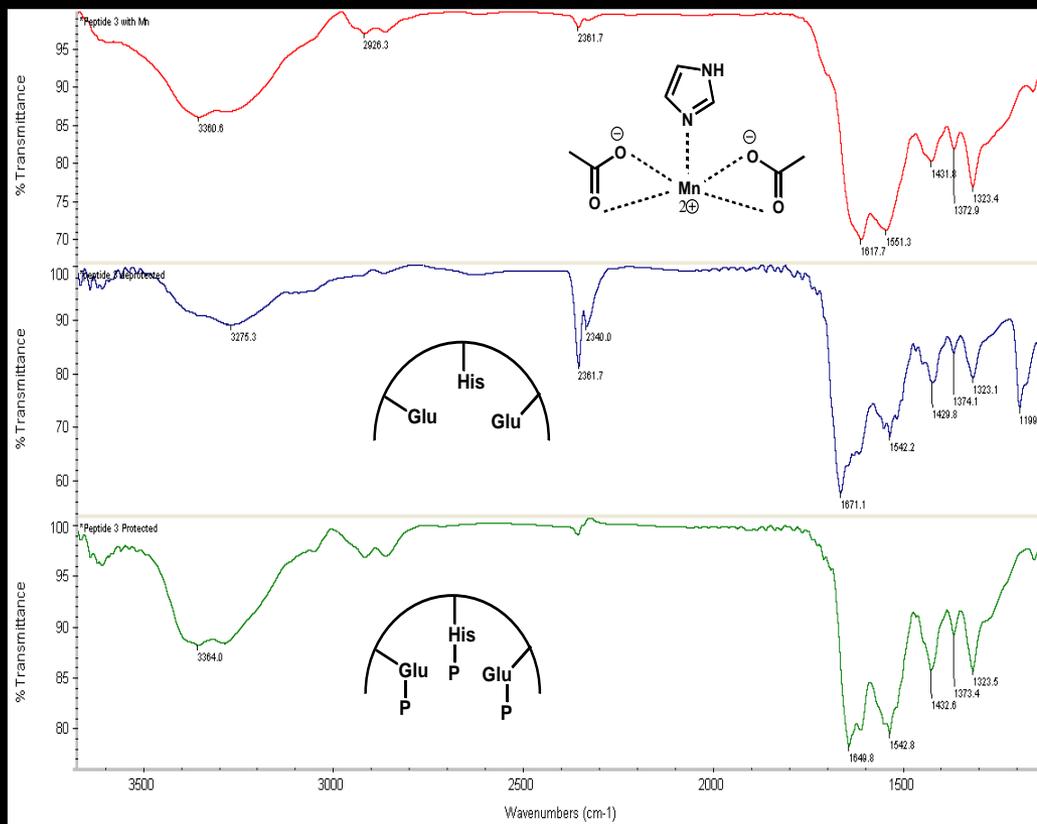


- Started with single Mn binding peptides, then designed and synthesized double binders. More recently established a collaboration with Bill Armstrong, Boston College, to incorporate Mn clusters into peptide designs.

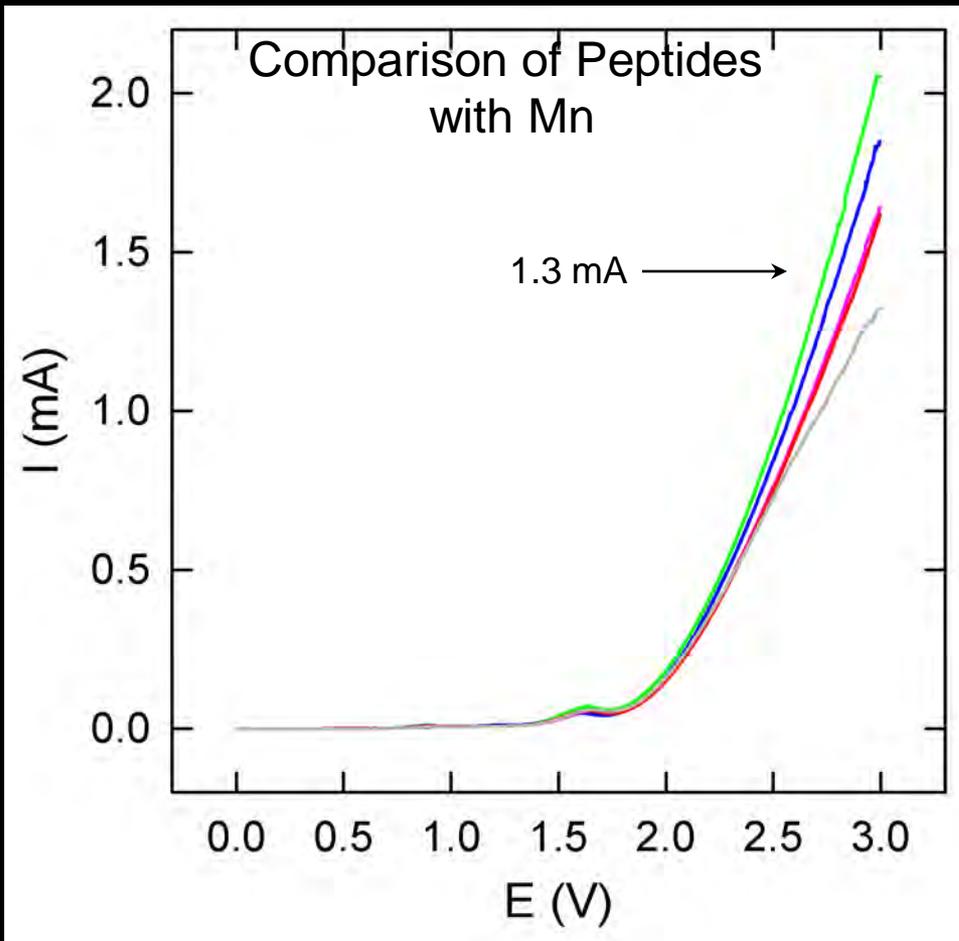
# Initial Mn-Binding Peptides



IR spectra showed that we were able to attach the peptides to the electrode surface, deprotect them and that they bound Mn. Control peptides did not bind Mn.



# Comparison of Electrolysis Currents



Change in potential at 1.3 mA compared to control (V)

peptide 2	-0.29
peptide 3	-0.23
polyHis	-0.15
peptide 1	-0.13
control	-

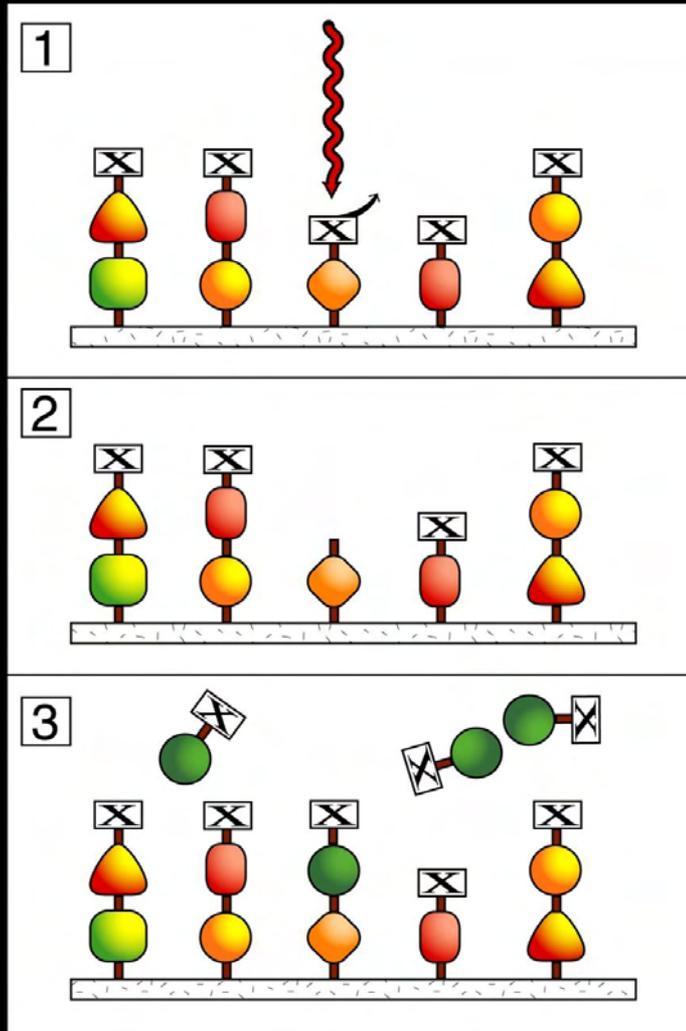
In terms of efficiency, one can see that it is possible with peptide 2 to get the same current (same rate of hydrogen production) at 2.7 V that would require 3.0 V with the control peptide. This is a 10% power reduction in that voltage range.

## Current Issue: Electrode surfaces not stable to chemical synthesis procedures

- Gold or Platinum Electrodes
- Polyindole Layer
- Peptide deprotection chemistry usually damaged surface
- Catalytic activity results were not reproducible

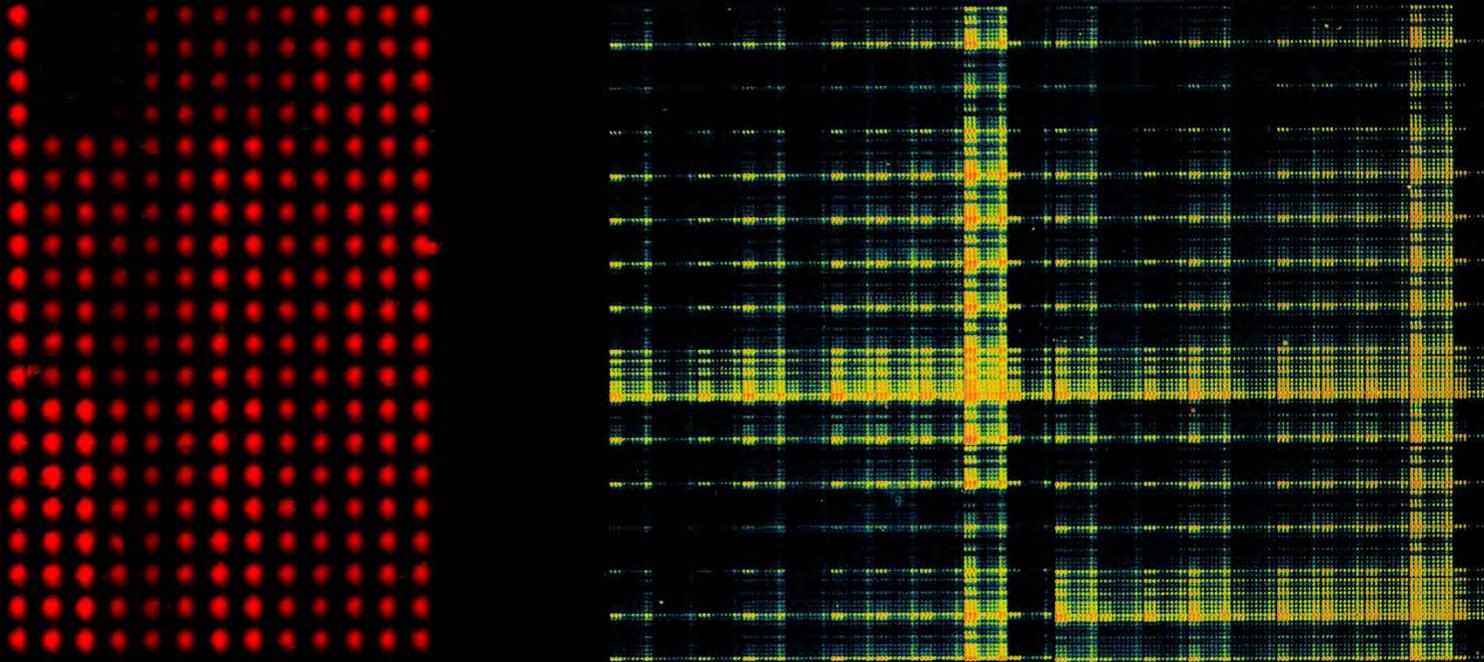


## RESULTS 2: Synthesize large arrays of peptide variants on electrodes



- Use chemical concepts developed in the DNA chip industry
- Can synthesize 10,000 – 1,000,000 specific molecules on a slide
- Assay each molecule in parallel
- Nearly unlimited chemical options
- Computationally aided design of each molecule
- Find out both what worked and what did not, allowing intelligent creation of subsequent libraries

# Using Light Directed Synthesis to Peptide Space



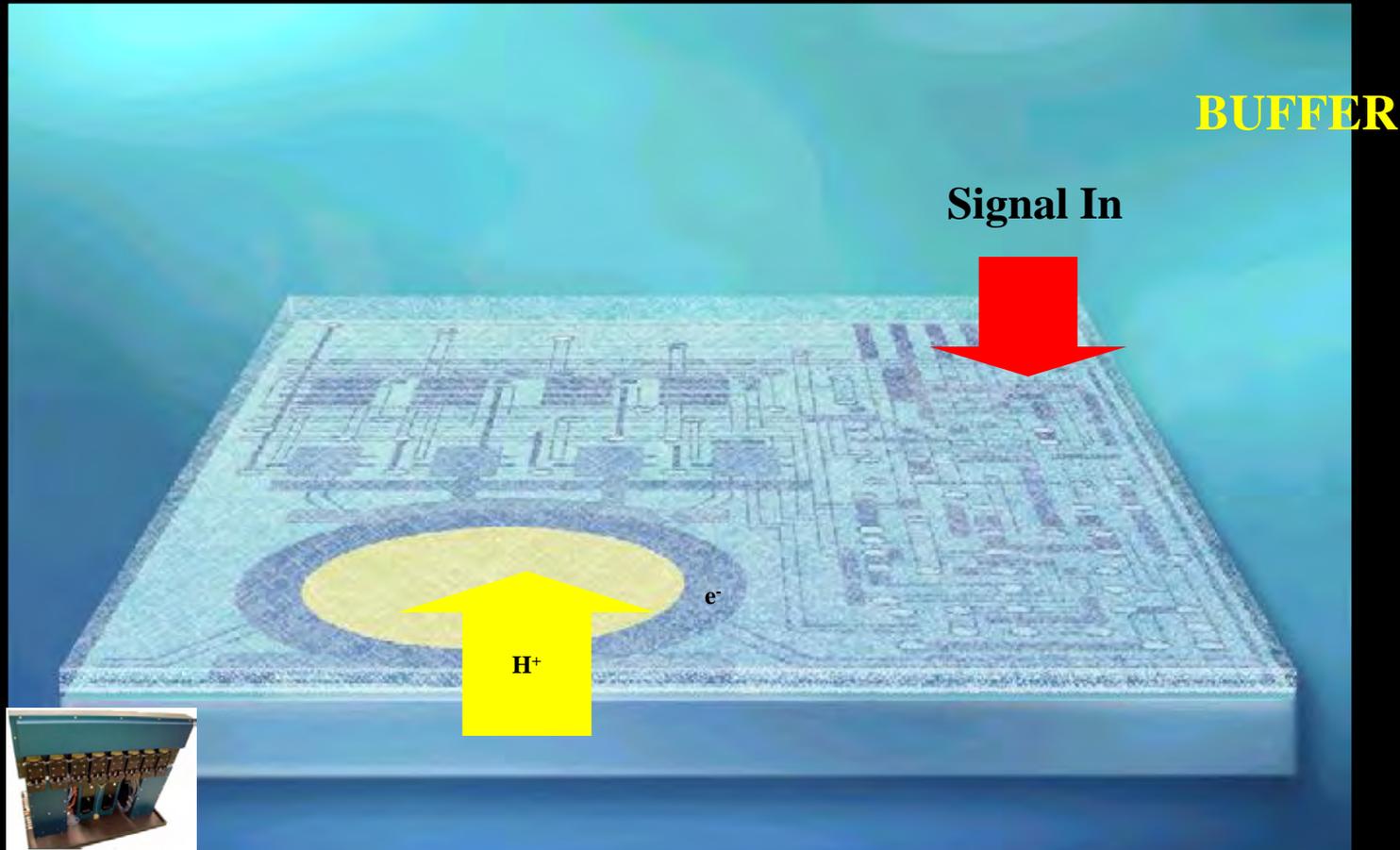
- Developed a system for generating tens of thousands of peptides on a slide
- Developed addressable arrays of electrodes for light directed synthesis

# Electrochemically Directed Synthesis

- Partnering with CombiMatrix
- This approach allowed direct synthesis on addressable electrodes
- As the chemistry worked about as well as light-directed, we decided to focus on this approach

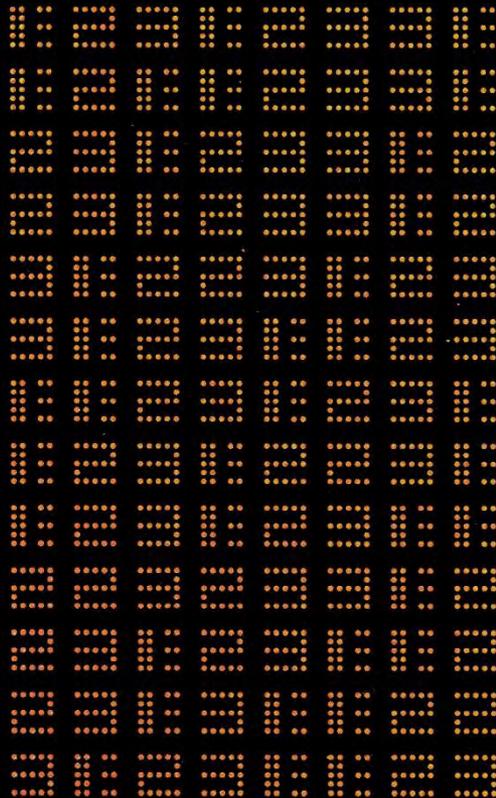


# CombiMatrix Chip Configuration



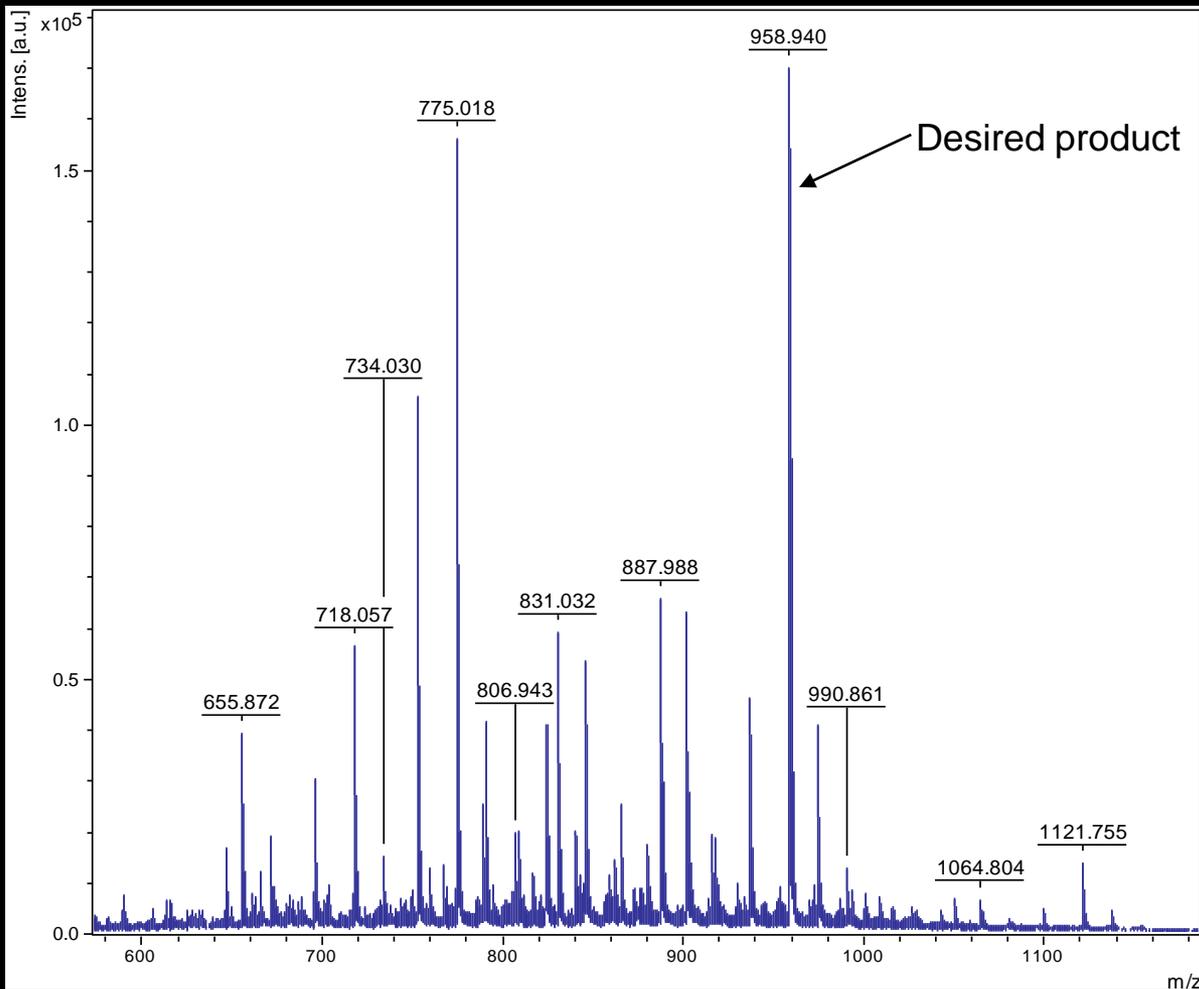
Electrochemically create an acid over a specific electrode that can be used for patterned chemistry

# Peptide Array Synthesis



- Top shows peptides of up to 10 amino acids synthesized on the CombiMatrix array
- Side show yield experiment giving stepwise yields of 94% using just glycine monomers

## More Complex Peptides: 70% Stepwise Yield and MALDI-Based Detection



As we moved to more complex peptide synthesis, we needed a more chemically informative analysis approach. We developed MALDI methods for direct detection, position sensitive from the chip surface.

## Current Status

- **The synthesis yields are good enough to make small arrays (hundreds) by combining a small number of electrochemical (variable amino acid) steps with standard Fmoc synthesis for the bulk of the peptide.**
- **The biggest synthesis problem we have is that the electrochemistry is not 100% orthogonal to the side chain protection chemistry. This results in side products when side-chain protected amino acids are present.**
- **We are exploring and comparing different conditions and different protection chemistries.**

## RESULTS 3: Characterize the activity of each of the metal binding peptides

- Each of the 12,000 elements in the array can be individually probed for electrochemical activity
- Current voltage measurements can be performed
- This allows electrochemical assays in array format



Initial work showing that the instrumentation was functional using electrocatalysis by horse radish peroxidase



## Future Work

- Check directly for metal binding on the chip
- Create an array of variants using electrochemical synthesis
- Vary a small number of positions in the amino acid sequence
- Minimize the effects of side chain protecting groups on the synthesis
- Repeat current measurements using the multi-Mn peptides
- New electrode surface preparation?

# Summary

- *Have designed metal binding peptides to use as starting sequences*
- *Have demonstrated the utility of light directed synthesis methods for creating libraries of peptides*
- *Have developed electrochemically directed synthesis of peptides with a limited number of side chains*
- *Have shown the ability to perform I/V measurements on the 12,000 CombiMatrix electrode chips*
- *Now trying to create arrays of variants and show optimization of electrocatalysis*