

The New Haven Local Section of the American Chemical Society Presents

The First Annual Undergraduate Research Symposium

Saturday, April 30, 2016

Hosted by
Southern Connecticut State University
Department of Chemistry and Office of STEM-IL



Symposium Schedule

We have students presenting from Quinnipiac, Yale, SCSU, UNH and Fairfield Universities

8:00 - 9:00	Registration Engleman Rotunda
9:00 - 9:05	Welcome and introductions EN* A120
9:05 - 9:50	Keynote speaker EH A120
10:00 - 10:45	Oral presentations EN A120
10:45 - 11:15	Coffee break EN B121A/B
11:15 - 12:20	Oral presentations EN A120
12:20 - 1:00	Lunch EN A121 A/B
1:00 - 2:00	Poster presentations <i>ASB* Floor 3</i> Tours of the Chemistry Department will be available
2:00 - 2:15	Awards ceremony ASB 222

*EN is Engleman, ASB is NEW Academic Science Building, Knuckle is the hallway between 2 sections of ASB.

Keynote Speaker

J. Michael McBride

Presentation Title

Non-Classical Crystal Growth and How a Sample Can Become Left-Handed

The classical view of single-crystal growth is that individual molecules or ions add one by one in the pattern defined by a pre-existing nucleus. More than a century ago an alternative mechanism was envisioned in which the units being added are themselves crystals. Although clever experiments in the 1930s supported such a “non-classical” mechanism involving oriented aggregation of independent crystals, it received little attention until the 21st Century. Now it has been demonstrated definitively. Kinetics for the classical mechanism is first-order in crystals and first-order in molecules or ions, but for oriented aggregation it is second-order in crystals. This higher order allows the kind of amplification of chiral purity that could explain emergence of homochirality in an achiral environment, a classical conundrum for the origin of life. It also underpins the phenomenon of Viedma ripening, which provides a new, simple approach for preparing single enantiomers.



Bio

J. Michael McBride has been on the faculty of Yale University since 1966 and currently serves as the Richard M. Colgate Professor of Chemistry Emeritus. Born in Lima, Ohio, McBride received his undergraduate education at the College of Wooster and Harvard College. He remained at Harvard for graduate study as an NSF Predoctoral Fellow and earned his Ph.D. for research on free radical chemistry under Paul. D. Bartlett. He joined the Yale faculty in 1966. The work of his group on organic solids has emphasized spectroscopic studies of free-radical reactions in single crystals, the relationship among molecular structure, reactivity, and the mechanical properties of organic solids, and the mechanisms of crystal growth and

dissolution. Prof. McBride was the recipient of the Swiss Prelog Medal in 1992, as well as the Nobel Laureate Signature Award in Graduate Education in 1987 and Catalyst Award of the Chemical Manufacturers Association in 1996 for his excellence in teaching at the graduate and undergraduate levels.

Corporate Sponsors

We would like to thank Gaussian and PerkinElmer for their generous donations and sponsorship of our symposium

Gaussian, Wallingford, CT



PerkinElmer, Shelton, CT



Thanks also to the American Chemical Society for the award of an Innovative Project Grant in support of the symposium

Oral Presentations

Time	Authors	Advisor	Academic Institution
10:00 – 10:20	Pranamya Dey Benjamin Rudshteyn Victor Batista <i>The Electronic Structure of an Intermediate in a Carbon Dioxide Reduction Reaction as Determined by Computational SFG Spectroscopy</i>	Victor Batista	Yale University
10:25 – 10:45	Brianna Kroon Elaine Pagliaro Brooke Kamrath <i>Evaluation of Microscopy and Vibrational Microspectroscopy for the Discrimination of Purple and Blue Nail Polishes</i>	Dr. Brooke Kamrath	University of New Haven
11:15 – 11:35	Natasha Kuegler Brooke Kamrath <i>Analysis and Characterization of Drug Microcrystals Using Raman Microspectroscopy and Fourier Transform Infrared Microspectroscopy</i>	Dr. Brooke Kamrath	University of New Haven
11:35 – 11:55	Jasmin Portelinha <i>Microbial Inhibition of Salmonella enterica Using Cinnamaldehyde and Polystyrene Fibers</i>	Dr. Nancy Savage Dr. Melanie Eldridge	University of New Haven
11:55 – 12:15	Albin Salazar Ericka Barnes <i>Definitive Assignment of Chemical Shifts in the 1H-NMR Spectrum of Syn-2,4-bis(4'-methylphenyl)-trans-1,3-di-thexyl)-di-1,3-boradi-2,4-azacyclobutadiene Using Computational Quantum Chemistry</i>	Ericka Barnes	Southern Connecticut State University

Poster Presentations

Group 1

Poster Number	Authors	Advisor	Academic Institution
1	Cody Edson	Dr. James Kearns	Southern Connecticut State University
	<i>Determination of Arsenic in Water with Silver Nitrate and Digital Image Analysis</i>		
3	Jason An	Dr. Dequan Xiao	University of New Haven
	<i>Integrative Discovery of Molecular Inhibitors to Ubiquitin C-Terminal Hydrolases for Studying Parkinson Diseases</i>		
5	Cessandra Guerrero	Todd R. Ryder	Southern Connecticut State University
	<i>Stereoselective Synthesis of α,α-Distributed Amino Acids as Arginase Inhibitors</i>		
7	Nicolas Carrasco Anna Larracuenta Maria White	Nicolas Carrasco	Quinnipiac University
	<i>Investigating the Kinetics of Glucoamylase in the Development of a Pollen Supplement for Honey Bees</i>		
9	Samantha Schrecke Kimberly DelBianco	Jillian Smith-Carpenter	Fairfield University
	<i>Synthesis and Characterization of Self-Assembling Nucleopeptides</i>		

Poster Presentations

Group 2

Poster Number	Author	Advisor	Academic Institution
2	Marianna Liang	Dr. Pier Cirillo Dr. Dequan Xiao	University of New Haven
<i>Towards the Synthesis of a Vibronically-Tunable Molecular Interferometer</i>			
4	Sadia Younas	Dr. Vincent T. Breslin Dr. James K. Kerns	Southern Connecticut State University
<i>Comparison of Cadmium Concentrations in Long Island Sound Harbor Sediment</i>			
6	Abigail Wiegand	Dr. Jiong Dong Pang	Southern Connecticut State University
<i>Testing Squash, Papaya, Corn and Soy Products in Connecticut for Genetic Modification</i>			
8	Christa Molé	Dr. Kent Marshall	Quinnipiac University
<i>A Study of Hydrophobic vs. Hydrophilic Components of Molecules in Acyclic Imide Preparation from C3 to C10</i>			
10	Nina Kosciuszek	Amanda Harper- Leatherman	Fairfield University
<i>Complementing electrochemical studies of self-organized gold nanoparticle~cytochrome c superstructures with UV-visible spectroscopy</i>			

ABSTRACTS

ORAL PRESENTATIONS

Presentation #1

The Electronic Structure of an Intermediate in a Carbon Dioxide Reduction Reaction as Determined by Computational SFG Spectroscopy

Pranammya Dey, Benjamin Rudshiteyn and Victor Batista (Yale University)
Advisor: Victor Batista

Recent research on the electrochemical reduction of CO₂ to CO has used sum frequency generation (SFG) methods to examine the low overpotential conversion pathway created by the co-catalysts 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) and silver. In this paper, we propose an electronic structure for the unknown reaction intermediate by using computational SFG combined with DFT geometry optimizations with comparison to the previously published experimental SFG spectra of the reaction intermediate. Vibrational spectra analysis shows a spectrum distinct from those of the starting materials and products. The orientation of the complex suggests a possible mechanism for the experimentally observed decrease in overpotential for CO₂ reduction and the improved selectivity for CO.

Presentation #2

Evaluation of Microscopy and Vibrational Microspectroscopy for the Discrimination of Purple and Blue Nail Polishes

Brianna Kroon, Elaine Pagliaro and Brooke Kammrath (University of New Haven)
Advisor: Dr. Brooke Kammrath

The purpose of this research is to evaluate the discriminating potential of microscopic and microspectroscopic methods for the analysis of blue and purple nail polish, which will impact the forensic science community by developing methodology for future cosmetic evidence. A total of 49 different polishes were analyzed using stereomicroscopy, brightfield microscopy, and polarized light microscopy for bottle identification then analyzed using Raman microspectroscopy and Fourier Transform infrared microspectroscopy for pigment and brand identification respectively. All 49 bottles of nail polish could be discriminated microscopically, based on various pigment characteristics. Raman microspectroscopy was successful in identifying two pigments, Pigment White 6 (anatase) and Pigment Blue 27; however, fluorescence prevented pigmentation identification in several samples. Infrared microspectroscopy was used for brand identification, with principal component analysis-canonical variate analysis (PCA-CVA) hold-one-out cross validation proving to have a 1.2% error rate. The results from this

research provide valuable information about cosmetic evidence for criminalists to use in investigations and adjudications.

Presentation #3

Analysis and Characterization of Drug Microcrystals Using Raman Microspectroscopy and Fourier Transform Infrared Microspectroscopy

Natasha Kuegler and Brooke Kammrath (University of New Haven)
Advisor: Dr. Brooke Kammrath

The purpose of this project is to determine if Fourier Transform Infrared (FT-IR) microspectroscopy and Raman microspectroscopy can be done on the product of drug microcrystalline tests in order to accurately identify drug samples, specifically bath salts (MDPV and ethylone), ephedrine, and a metabolite of cocaine (ecgonine). Drugs are involved in many cases of criminal activity. With such a backlog of evidence a quick, accurate, cost effective, and non-destructive method would be useful for forensic analysis. The Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) requires that multiple techniques not based on the same property of a substance must be used in order to obtain acceptable results. Raman microspectroscopy and FT-IR with microcrystalline tests meet these requirements. Microcrystals were successfully grown for MDPV and ephedrine. FT-IR and Raman microspectroscopy successfully identified the two drug samples.

Presentation #4

Microbial Inhibition of Salmonella enterica Using Cinnamaldehyde and Polystyrene Fibers

Jasmin Portelinha (University of New Haven)
Advisors: Dr. Nancy Savage and Dr. Melanie Eldridge

Salmonella enterica is a gram negative, rod shaped bacteria that commonly causes foodborne illnesses. S. enterica readily adheres to surfaces where it typically grows biofilms. Biofilms are layered bacterium living in a symbiotic community. Bacteria are more resistant to antimicrobial agents when they live in biofilms. This research aims to use electrospun polystyrene films impregnated with cinnamaldehyde to inhibit S. enterica biofilm growth. Essential oils, such as the oil of cinnamon with the active ingredient cinnamaldehyde, have been effective in inhibiting Salmonella biofilm growth. Growth studies were performed on electrospun polystyrene and cinnamaldehyde-impregnated polystyrene films to determine if incorporating cinnamaldehyde in plastics would inhibit biofilm growth. Electrospun films deposited on glass slides were exposed to S. enterica inoculated media and biofilm growth was monitored over time. Three different growth conditions were examined. Some films were kept in the inoculated media for the entire test period, some were moved to fresh media and some were removed from media entirely. Films grown under each set of conditions were fixed in cold methanol and stained with 0.4% methylene blue dye to stop biofilm growth at different time periods. The samples

were analyzed using the Hitachi 3010-U UV-Vis spectrometer to quantify the bacteria on the films. Data will be presented which shows the extent of biofilm inhibition with and without cinnamaldehyde under the various growth conditions.

Presentation #5

Definitive Assignment of Chemical Shifts in the 1H-NMR Spectrum of Syn-2,4-bis(4'-methylphenyl)-trans-1,3-di-thexyl)-di-1,3-boradi-2,4-azacyclobutadiene Using Computational Quantum Chemistry

Albin Salazar (Southern Connecticut State University)
Advisor: Ericka Barnes

Nuclear Magnetic Resonance (NMR) spectroscopy is the most dominant characterization technique in chemical synthesis. The complete assignment of chemical shifts or resonances in the experimental 1H-NMR spectrum of a cyclodiborazane molecule (Figure 1) and its derivatives has been made particularly challenging owing to the unhindered rotation about single carbon-carbon bonds, in particular, those within the thexyl groups attached to the boron atoms in the four-membered cyclodiborazane ring. Current research has been unable to definitively assign a specific thexyl group to a particular set of NMR resonances. The most abundant conformations will be computed and identified by molecular mechanics software (PCmodel®), while Boltzmann-averaged energies and chemical shifts of the most abundant conformations will be refined by quantum mechanical (Gaussian®) NMR calculations. Theoretical chemical shifts will then be compared to those in the experimental proton spectrum to aid in the assignment of resonances.

POSTER PRESENTATIONS

Poster #1

Determination of Arsenic in Water with Silver Nitrate and Digital Image Analysis

Cody Edson (Southern Connecticut State University)
Advisor: Dr. James Kearns

Arsenic is a natural occurring, carcinogenic metalloid found within the Earth's crust. As a result of its natural abundance, as well as its geochemistry, many sources of ground water are contaminated with varying concentrations of arsenic. Current field tests are able to test for concentrations of arsenic above 20 ppb by reacting arsine gas (formed through a reaction with sulfamic acid and zinc) with mercuric bromide to form a discoloration on a test strip. The intensity of the discoloration is directly related to the concentration of arsenic within the sample, and therefore can be compared to a color scale provided with the kit. These test have shown to be effective at measuring concentrations ≤ 20 ppb (parts per billion); however, the W.H.O world standard for arsenic in groundwater is 10 ppb.

Therefore, these tests are ineffective at quantifying trace amounts of arsenic. A method was created using 0.4% silver nitrate, dissolved in 1.0 % concentrated nitric acid and water solution in place of mercuric bromide in order to create a discoloration on the test strip. The discoloration was then scanned to a computer, and the blue color intensity values of the discoloration were measured, as the concentration of arsenic is inversely related to intensity of blue color. Finally, using 95% confidence, concentrations of 0, 5, and 10 ppb were shown to be statistically different. This data supports that silver nitrate is capable of determining concentrations at the 95% confidence level, below 10 ppb, which is important in order to determine the safety of drinking water in water scarce areas.

Poster #2

Towards the Synthesis of a Vibronically-Tunable Molecular Interferometer

Marianna Liang (University of New Haven)
Advisors: Dr. Pier Cirillo and Dr. Dequan Xiao

The field of molecular electronics or nanoelectronics seeks to develop molecular-scale devices and thus reach the ultimate level of miniaturization. In 2009, Xiao et al proposed a molecular interferometer where the electron transfer through the molecule is vibronically tunable due to the interference of vibronic transfer pathways. According to this phenomenon, an electron can be transferred from the electron donor end of the molecule to the electron acceptor end by exciting specific vibrational modes, which can be implemented by the excitation of IR or visible light in experiments. We propose to synthesize such molecular interferometers, and describe here the planned scheme and progress towards the synthesis of such molecules. Our work will lead to the experimental verification of molecular interferometers and provide new insights for the design of molecular electronic devices.

Poster #3

Integrative Discovery of Molecular Inhibitors to Ubiquitin C-Terminal Hydrolases for Studying Parkinson Diseases

Jason An (University of New Haven)
Advisor: Dr. Dequan Xiao

Parkinson disease is a progressive neurological disorder that eventually leads to the loss of physical functions of human body. Parkinson disease affects up to 1 million Americans, and 10 million people in the world. However, currently there is no cure for the disease, partially due to the lack of knowledge of the entire molecular pathology. Ubiquitin carboxyl-terminal hydrolase L1 (UCHL1) is an enzyme that is abundantly and selectively expressed in neurons, and abnormal expression (e.g., mutation) of UCHL1 is found to be associated with Parkinson disease, cancers (e.g., lung, colorectal, and pancreatic cancers), and tumor progression. Several potent inhibitors were discovered for UCH-L1 mutants and showed positive results in the suppression of tumor progression. However, the molecular

interaction mechanism remains unclear, and more effective inhibitors are demanded. To understand the molecular interaction mechanism between UCHL1 and inhibitors, we proposed to integrate computational chemistry, quantum chemistry, and experimental synthesis methods to discover novel and effective inhibitors for UCHL1. Through the docking of several known inhibitors and non-inhibitors onto the UCHL1 protein using computational chemistry methods, we successfully identified the active inhibition site of UCHL1, and thus revealed the detailed molecular interactions between UCHL1 and the inhibitors. Through ab initio quantum chemistry analysis of the binding structures between UCHL1 and inhibitors, we proposed a couple of novel inhibitors that were proved to be more effective by calculations. Hence, we synthesized the proposed new inhibitors that are testable by chemical biology methods in experiments.

This is the first work that integrated computational chemistry, quantum chemistry, and experimental synthesis methods for designing UCHL1 inhibitors. Our work provided significant new insights at the molecular level for the inhibition of UCHL1 proteins, which may lead to the discovery of effective drugs for the cure of the Parkinson diseases associated with abnormal expression of UCHL1 proteins.

Poster #4

Comparison of Cadmium Concentrations in Long Island Sound Harbor Sediment

Sadia Younas (Southern Connecticut State University)
Advisors: Dr. Vincent T. Breslin and Dr. James K. Kerns

Cadmium is a non-nutritive trace metal and is classified as a Group B1 carcinogen (probable human carcinogen) by the EPA. Cadmium poses an even greater risk to aquatic organisms. It is exceptionally toxic even at low concentrations and results in acute and chronic effects on aquatic organisms. The goals of this study were to examine spatial trends in sediment cadmium concentrations in Black Rock and Stonington harbors and to determine the covariance of cadmium with respect to other physical (grain-size and organic content) and chemical properties (copper, iron and zinc) of the sediment. Cadmium concentrations were measured using electrothermal atomic absorption spectroscopy whereas copper, iron and zinc concentrations were detected utilizing the flame atomizer. Results show cadmium concentrations in both harbors were highest in the inner (northern) harbor regions and decreased in the outer (southern) regions of each harbor. Although sediment cadmium concentrations in Stonington harbor surpass the crustal abundance (0.1 mg/kg) they are well below the NOAA sediment toxicity threshold (ERL limit 1.2 mg/kg), largely due to the rural setting of the harbor. In contrast, Black Rock Harbor is heavily industrialized, with the mean cadmium concentrations of inner Black Rock harbor stations exceeding the NOAA ERM toxicity threshold (9.6 mg/kg), with two inner harbor stations reporting values of >22 mg/kg cadmium. Sediment cadmium concentrations in both harbors directly vary with sediment organic carbon content (LOI) and other sediment metals (copper, zinc and iron).

Poster #5

Stereoselective Synthesis of α,α -Distributed Amino Acids as Arginase Inhibitors

Cassandra Guerrero (Southern Connecticut State University)

Advisor: Todd R. Ryder

Arginase is a manganese-containing enzyme that catalyzes the hydrolysis of L-arginine to yield urea and L-ornithine. It competes with nitric oxide synthase by depleting L-arginine from their common substrate pool, thus affecting downstream NO-dependent activities such as regulation of blood pressure and smooth muscle tone. In addition, it has recently become appreciated that arginase inhibitors may also be useful for cancer immunotherapy. For example, arginase is overexpressed in myeloid-derived suppressor cells (MDSC), resulting in low levels of arginine in the tumor microenvironment and decreased activity of T- and natural killer cells. An arginase inhibitor is expected to enter clinical trials for cancer in the summer of 2016. The most potent arginase inhibitors in the literature are α,α -disubstituted arginine analogs with a boronic acid warhead in place of the substrate aminoguanidine. The stereoselective synthesis of these compounds is challenging, particularly for analogs with bulky α -substituents that preclude alkylation of a chiral glycine derivative. As an alternative, we are investigating the enzyme-catalyzed desymmetrization of a meso diester to install the amino acid stereocenter. This approach has several potential advantages, including wide substrate scope and environmentally-friendly reaction conditions.

Poster #6

Testing Squash, Papaya, Corn and Soy Products in Connecticut for Genetic Modification

Abigail Wiegand (Southern Connecticut State University)

Advisor: Dr. Jiong Dong Pang

The information on the abundance of genetically modified organisms or foods (GMOs) in Connecticut is lacking, which is consistent with the rest of the United States. The public opinion on the use of the GMOs, especially for human consumption, is mixed. In 2013, Connecticut was the first state in the country to enact a law requiring that foods be clearly labeled on the retail package as to whether they contain GMOs. However, the CT law was written so that it would not go into effect until a certain number of states passed similar legislations. This seems to have catalyzed a reaction over the past few years, since recently Vermont and Maine have also passed similar mandatory labeling laws. The current research tested the abundance of GMOs available for consumer purchase in CT and therefore added to the body of scientific data on the abundance of GMOs in consumer products in CT and beyond.

Poster #7

Investigating the Kinetics of Glucoamylase in the Development of a Pollen Supplement for Honey Bees

Nicolas Carrasco, Anna Larracuenta and Maria White (Quinnipiac University)
Advisor: Nicolas Carrasco

With the recent decrease in honeybee population, more focus has been placed on the preservation of healthy honeybees by investigating the effects of pesticides, environmental changes, and disease. To aid in this effort, we are investigating the development of a pollen supplement diet for honey bees. This supplement contains a combination of carbohydrates, proteins, fats, vitamins, and minerals. We will demonstrate our ongoing efforts via the preparation of a pollen supplement using a 3:2:2:1:1 ratio of oat, corn, wheat, brown rice, and barley, respectively. Once the sample supplement was mixed, we showed the kinetics for the enzymatic digestion of starch using both α -amylase and glucoamylase. Results show that the glucoamylase worked more effectively, at a faster rate, and broke starch down into glucose building blocks. Starch, at concentrations above 3% in the diet, can be toxic to honeybees. The current focus of this study includes starch-iodine and colorimetry results to show the disappearance of starch as a function of time, as well as the formation of glucose. These preliminary results suggest that glucoamylase can be used for the development of a pollen supplement for honey bees.

Poster #8

A Study of Hydrophobic vs. Hydrophilic Components of Molecules in Acyclic Imide Preparation from C3 to C10

Christa Molé (Quinnipiac University)
Advisor: Dr. Kent Marshall

A study to determine when the hydrophobic portion of molecules overrides the hydrophilic portion during symmetrical acyclic imide synthesis was carried out from C3 to C10. The corresponding alkyl nitriles and alkyl carboxylic acid anhydrides were used. The reactions were catalyzed by silica sulfuric acid (1) and were carried out at 80 deg C. The study used percent yield of the solid imides as a measure of whether the reaction went or not. The imide products were confirmed by a GC-MS comparison of the m/z value of the molecular ion to the MW of the imide. C3 to C6 had relative high product yields, ranging from 19.0 to 66.7%, however, C7 to C10 were at or near zero. The data clearly indicated the reactivity wall was at C7. These results were consistent with previous work using a different set of reagents (acid chloride, amide and acid anhydride).
(1) Z. Habibi, et al., SYNLETT, 2007. 5, 812.

Poster #9

Synthesis and Characterization of Self-Assembling Nucleopeptides

Samantha Schrecke and Kimberly DelBianco (Fairfield University)

Advisor: Jillian Smith-Carpenter

In the complex environment of cells, biomolecular structures have evolved a delicate balance between stability and dynamic responsiveness. Both of these factors rely on the strength and diversity of non-covalent interactions. In an effort design more responsive biomaterials, we have integrated the recognition elements of nucleic acids with self-assembling peptides. Herein, we report the synthesis of guanosine modified short peptides (nucleopeptides) and the characterization of the resulting supramolecular structures assembled in various conditions. Infrared spectroscopy (IR) is used to identify the major secondary structures, G-quartets and extended β -sheet formations, while Atomic Force Microscopy (AFM) is used to image the supramolecular fibers that form. Information from these self-assembling nucleopeptide studies will extend current strategies for “bottom-up” control of final morphology.

Poster #10

Complementing electrochemical studies of self-organized gold nanoparticle~cytochrome c superstructures with UV-visible spectroscopy

Nina Kosciuszek (Fairfield University)

Advisor: Amanda Harper-Leatherman

The addition of the protein, cytochrome c (cyt. c), to gold nanoparticles in solution results in self-organization of cyt. c into multilayered protein superstructures (abbreviated as Au~cyt. c superstructures) and stabilizes the thousands of organized cyt. c proteins to unfolding both when encapsulated in porous solids and when remaining in solution. Our research has shown that the electrochemical characteristics of superstructure-assembled cyt. c are enhanced compared to cyt. c alone. In order to determine whether the enhanced electrochemical properties are directly related to multiple protein layers staying intact at the electrode surface, protein superstructures were stripped from electrode surfaces and were measured with UV-visible spectroscopy. These results will aid in the development of future bioanalytical devices when a good understanding of the interaction between protein and material surface is needed.

Thank you

A special thanks to:

The faculty and staff at Southern Connecticut State University
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Dr. Christine Broadbridge, Director of the Office of STEM-IL

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