MULTIFUNCTIONALITY

The fabrication of multifunctional materials with tunable structure and properties requires programmed binding of their building blocks. For example, particles organized in long-ranged structures by external fields can be bound permanently into stiff chains through electrostatic or van der Waals attraction, or into flexible chains through soft molecular linkers such as surface-grafted DNA or polymers.

Read more about this Research from the Rubinstein Group, published in Nature Materials.

-Continued on Page 8

PHOTOREDOX CATALYSIS

Over the past several decades, organometallic cross-coupling chemistry has developed into one of the most reliable approaches to assemble complex aromatic compounds from preoxidized starting materials. More recently, transition metal–catalyzed carbon-hydrogen activation has circumvented the need for preoxidized starting materials, but this approach is limited by a lack of practical amination protocols. In a paper published in Science, researchers in the Nicewicz Group present a blueprint for aromatic carbon-hydrogen functionalization via photoredox catalysis and describe the utility of this strategy for arene amination.

-Continued on Page 9

3D Manufacturing for the Future

Chancellor’s Eminent Professor Joseph DeSimone has a knack for starting companies. His breakthroughs as a polymer chemist have led to multiple successful entrepreneurial ventures in green chemistry, medical devices, nanomedicine, and now, with his colleagues Dr. Alex Ermoshkin and Cary C. Boshamer Professor of Chemistry Ed Samulski, in 3D printing.

On March 16th of this year, DeSimone revealed his most recent undertaking on the TED2015 stage in Vancouver, where he delivered a talk on a new 3D printing technology called Continuous Liquid Interface Production, or CLIP, which is being developed by his new Silicon Valley-based company, Carbon3D. That very same day, the CLIP technology was featured on the cover of Science.

-Continued on Page 8

Morehead Laboratories a Chemistry Engine

Chemistry is fundamental to all areas of modern science and technology, providing a foundation for fields such as biochemistry, chemical engineering, food science, materials science, geology, nanotechnology, pharmacology, medicine, and dentistry. Moreover, the laboratory experience is a critical part of any science education.

-Continued on page 9

Valerie Ashby new Dean at Duke

We are extending our heartfelt congratulations to Professor and former Chair Valerie Ashby, who left us in July to become the new Dean of Arts and Sciences at Trinity College at Duke University. As she unflaggingly did here at Carolina, she will most assuredly bring her outstanding leadership and charisma to that school. We are of course disappointed to see her go but are grateful for all that she did for us here at the Department of Chemistry. We wish her well in her new endeavor. In her new position, Ashby will oversee the university’s main academic units across the arts, humanities, social sciences and natural sciences.
F or those of you expecting an annual Chair’s message from Professor Valerie Ashby, do I have news for you! In July, 2015, Valerie became the Dean of Trinity College of Arts & Sciences at Duke University. Anyone who witnessed Valerie’s administrative prowess, problem solving skills, and inimitable personal touch, will immediately grasp and appreciate our Blue Devil colleagues’ excitement at bringing Valerie to the other side of I-40. Once and always a Tar Heel, Valerie remains a cherished member of our Carolina family. We are excited to watch her bring her creativity, energy, and unflagging optimism to her new duties at Duke.

Unto the breach stepped our colleague Joseph Templeton to assume Chair duties on an interim basis. Joe’s service to the Department and University has been well documented in these pages. With a great deal of personal gratitude I am pleased to publicly convey my sincere thanks and appreciation for his willingness to step into this critical position until a new Chair was elected. Joe will leave the Chair’s office at the end of the year, and will then lead a dynamic group of UNC undergraduates during their study abroad seminar in London. All of which leads us to your humble narrator. I have been elected to become the new Department Chair, starting January first, and am very excited to lead the Chemistry Department in this new capacity. I am happy to call UNC home since July 2001 and am keen to build on the storied traditions of our department. Certainly it is a pleasure for me to compose this letter to you from the beautiful Science Complex on Polk Place to apprise you of the year’s activities.

October brings lovely fall weather to Chapel Hill and also ushers in Nobel season. At this writing, Carolina is still basking in the glow and champagne cork pops of its second-ever Nobel Prize. Professor Aziz Sancar was one of three 2015 Chemistry Nobel Laureates for his groundbreaking work on the DNA repair system in cancer cells.

The external recognitions for the work of my talented Chemistry colleagues have come in at an impressive clip since our last communication to you. We recently learned that Professor Jillian Dempsey was chosen for a prestigious 2015 Packard Fellowship in Science and Engineering. To gain a sense of this accomplishment, please note that only eighteen scientists in all fields are chosen as Packard Fellows in a given year. Also, this marks the third straight year that a UNC Chemistry faculty member has been named to this elite cohort. The award carries with it $875,000 in unrestricted research funds.

Professors Leslie Hicks and Eric Brustad learned this fall that they will be recipients of five year National Science Foundation CAREER awards to help drive their exciting nascent programs in mass spectrometry and directed chemical evolution, respectively. Professor Marcey Waters was awarded this year’s Mary Turner Lane award in honor of her outstanding contributions to the lives of women students, faculty, staff and administrators at Carolina.

Professor Joseph DeSimone was the inaugural recipient of the Kabiller Prize in Nano-science & Nanomedicine from Northwestern University’s International Institute for Nanotechnology. The award carries with it a prize of $250,000. If you Google “DeSimone TED talk,” you can see him speak about a very interesting 3D printing endeavor mentioned in this newsletter.

We are very proud to announce Kaitlyn Tsai’s selection as a Barry Goldwater Scholar. The Barry Goldwater Scholarship Program was established by Congress in 1986 to honor Senator Barry Goldwater, who served his country for 56 years as a soldier and statesman, including 30 years of service in the U.S. Senate. The purpose of the Goldwater Foundation is to provide a continuing source of highly qualified scientists, mathematicians, and engineers by awarding scholarships to college students who intend to pursue research careers in these fields.

Kaitlyn Tsai is from Apex, North Carolina where she went to Apex High School. She feels that choosing chemistry was one of the best decisions she could have made for her undergraduate studies. She claims that “between the amazing faculty and extensive opportunities for research,” she has “become more inspired to pursue chemistry research.” Her initial choice was to start as a Chemistry B.S. major, but after taking genetics, she became more interested in the biological applications of chemistry and switched to the biochemistry track. Kaitlyn is currently conducting research in Dr. Marcey Waters’ Bioorganic Chemistry lab, where she is part of a team investigating protein binding involved in histone methylation for epigenetic regulation. After graduation, Kaitlyn intends to enroll in a Ph.D. program in Chemistry, and hopes to continue epigenetic research. She would also like to stay in academia since it would give her the opportunity to teach and mentor.
Congratulations to Assistant Professor Jillian Dempsey, on being awarded a 2015 Packard Fellowship for Science and Engineering! The Packard Fellowships program invests in future leaders who have the freedom to take risks, explore new frontiers in their fields of study and follow uncharted paths that can lead to groundbreaking discoveries. It is among the nation’s largest non-governmental fellowships. The award from the David and Lucile Packard Foundation is for $875,000 over five years, and is awarded to “highly creative researchers early in in their careers.”

“Since arriving in Chapel Hill in 2012, Jillian Dempsey has tackled the looming energy problem with intelligence and intensity,” said Joe Templeton, Venable Professor and Interim Chair of the Department of Chemistry. “Her investigations of synchronous and asynchronous proton and electron movements are leading the way to new sunlight-to-energy conversion opportunities.”

Dempsey and her lab are searching for ways to efficiently capture sunlight in artificial systems and carry out fuel-producing reactions to store the sun’s energy in the high-energy chemical bonds of molecules like hydrogen. Her work is contributing to a growing need to develop renewable, environmentally friendly energy sources.

Nicewicz Hettleman Prize

Professor David Nicewicz has been awarded the Phillip and Ruth Hettleman Prize for Artistic and Scholarly Achievement by Young Faculty. Nicewicz has created a groundbreaking set of advances in the formation of small molecule building blocks by the artful marriage of low-energy light and suitably chosen organic dyes. This combination activates common organic structures in unique ways and enables novel transformations that had eluded the research community before.

Nicewicz, who earned his doctorate in chemistry from Carolina in 2006, conducted postdoctoral training at Princeton, where he discovered and began developing the utility of photoredox catalysis in stereoselective organic synthesis. Stereoselective synthesis permits chemists to assemble small molecule building blocks with the carbon, nitrogen and oxygen functional groups displayed in a defined three-dimensional orientation. This feature is critical to the bioactivity of organic molecules.

David returned to Carolina in 2009 to join the faculty at the chemistry department and continue this trailblazing work.

Waters Wind AWFP Award

Marcy Waters, Gordon and Bowman Gray Term Professor of Chemistry, has won the 2015 Mary Turner Lane award in honor of her outstanding contributions to the lives of women students, faculty, staff and administrators at Carolina. The Association for Women Faculty and Professionals presented the award to Waters this spring.

Waters, who holds a Gordon and Bowman Gray Term Professorship for excellence in teaching, also received a 2014 Tanner Award for Excellence in Undergraduate Teaching. In student citations for that award, Waters was described as “the epitome of what I value in a professor,” and “the soul and spirit” of undergraduate teaching. One student said of her, “Dr. Waters is who I want to be when I grow up.”

DeSimone Awarded First Kabiller Prize

Northwestern University’s International Institute for Nanotechnology, IIN, announced on September 30th that chemist Joseph M. DeSimone of the University of North Carolina at Chapel Hill is the recipient of the inaugural $250,000 Kabiller Prize in Nanoscience and Nanomedicine. The Kabiller Prize was established by the IIN earlier this year through a generous donation from Northwestern trustee and alumnus David G. Kabiller. Recipients are selected by an international committee of experts in the field.

“These awards were established not only to recognize the people who are designing the technologies that will drive innovation in nanomedicine, but also to educate and shine a light on the great promises of nanomedicine,” said Kabiller, co-founder of AQR Capital Management, a global investment management firm in Greenwich, Connecticut.
The Department’s Diversity Committee led a successful application effort to become a three-year National Science Foundation Research Experience for Undergraduates, NSF REU, site. We welcomed our first cohort of students this summer, a wonderful and diverse group of dedicated and hardworking students from, inter alia, Morehouse University, North Carolina A&T, and the University of Puerto Rico. We are hopeful that we “set the hook” with some of these students and that we will see graduate applications from these future stars. We look forward to welcoming our second cohort in the summer of 2016.

On behalf of all my colleagues, please allow me to convey our sincere thanks for taking the time to read our newsletter and “catch up” with Carolina Chemistry. The exciting developments described herein are driven by an incredible collection of young and young-at-heart scholars. The Chair is regularly approached with exciting opportunities and ideas; his or her capacity to approve these initiatives is intimately linked to available resources. Valerie’s initiation of the “Say Yes” fund provides an opportunity for you to contribute resources that have a tangible impact on bringing student and faculty initiatives to fruition. In this spirit, we invite you to consider contributing to the “Say Yes” fund — your gift makes a difference!

We always enjoy hearing from friends of Chemistry. Please feel free to contact us with news or to stop by the Department if your travels bring you to Chapel Hill.

With Best Regards,

Jeff Johnson
Assistant Professor James Cahoon had some very rewarding months this year. First, he was chosen as one of eighteen national recipients of a David and Lucile Packard Foundation Fellowship. He was elected as one of the nation’s most innovative early-career scientists and engineers receiving a Packard Fellowships for Science and Engineering. Each Fellow will receive a grant of $875,000 over five years to pursue their research. “The Packard Fellowships are an investment in an elite group of scientists and engineers who have demonstrated vision for the future of their fields and for the betterment of our society,” said Lynn Orr, Keleen and Carlton Beal Professor at Stanford University, and Chairman of the Packard Fellowships Advisory Panel.

As if that was not enough, he was then awarded a Sloan Research Fellowship by the Alfred P. Sloan Foundation. Given annually since 1955, the fellowships go to early career scientists and scholars whose achievements and potential identify them as rising stars, the next generation of scientific leaders. “These fellowship provide a well-deserved recognition of Jim’s accomplishments and will help him continue his active research program,” said Valerie Ashby, Professor and former Chair of the Chemistry Department. “I have no doubt that his research efforts will be the source of major breakthroughs in the field of semiconductor nanomaterials and their exciting applications.”

Finally, James learned that he is one of 48 recipients of an Award from the Research Corporation for Science Advancement, RCSA, which supports “innovative research projects proposed by early career scientists at American colleges and universities.” The awards cover a wide range of research in astronomy, chemistry, and physics. “RCSA has always been about finding and supporting the next big scientific paradigm, the theory or discovery that will revolutionize and advance an entire field of study,” said RCSA President Robert N. Shelton. All RCSA awards are subject to a critical peer-review process, which tends ensure that funding goes to the best and brightest among America’s young academic scientists, the men and women who are likely to be leaders in their fields in the coming decades. Over the past century, 40 scientists receiving RCSA support have also earned the Nobel Prize, and many others have received significant honors in the physical sciences.
Why I Give to Carolina Chemistry

Dr. Gordon E. Cadwgan received his Bachelor of Science degree in Chemistry from the University of North Carolina, Chapel Hill, in 1967 and holds a Ph.D. in Analytical Chemistry, 1975, from the University of Massachusetts in Amherst, MA.

Please tell us a little bit about your career and what you are currently up to.

After graduating from UNC in 1967 I spent three years in the U.S. Army and then returned to Boston where my parents lived. For a while, I searched for a job, but then, after taking some summer courses at Boston University, decided I would go back to school to pursue a Doctorate in Chemistry. I was not sure if I had the ability for that endeavor; I had been away from Chemistry for 3 years, and probably forgotten more than I knew. I called Dr. Charles Reilly, my Analytical Chemistry teacher at UNC, and asked if he could recommend a good school for Analytical Chemistry. Among others, he mentioned UMASS at Amherst, which would be perfect for me. Low, in-state tuition, close to home, great location, teaching assistant possibilities, and overall a good department. Five years later, after a lot of hard work and fun, I left UMASS with a Ph.D. in Analytical Chemistry.

My first job, 1975, was with Union Carbide in Charleston, WV. I worked with a small group of engineers and chemists trying to make basic chemicals, used as building blocks for larger molecules, from “synthesis” gas. This was the time of the energy crunch and synthesis gas was a cheap byproduct derived from burning cheap oil residue or coal. We visited a number of companies world-wide with a fully equipped laboratory and synthesis plant in a semi-trailer to see if their synthesis gas would work in our production facilities. Great fun! I loved working in refineries and chemical plants. I participated in lots of interesting chemistry and exciting powerful processes, leading to really great products.

After five years with Union Carbide, I went to DuPont in Wilmington, DE, wanting to get closer to my New England roots, and worked in their Agricultural Products Department. I did not realize how big it would become, but just beginning in 1980, there was a revolution in agricultural chemicals, involving the development of very low use-rate and low volume herbicides and fungicides. This truly revolutionized the growing of food everywhere and also helped propel the department from a 100 million dollar business to a billion dollar business in ten years. If you are going to work for a company, choose one which is growing rapidly. You will never have a dull moment with new people, new ideas, new products, and lots of money.

So not everything works out as one might expect. In 1992 I was diagnosed with a genetic condition which, like emphysema, causes destruction of lung tissue and a decline in lung function. Usually, once diagnosed, the decline accelerates leading to respiratory infections and an inability to do any work or play which requires lung power. I retired on disability in 1996 at age 52. My wife, Ruth, who also worked for DuPont, worked for another 3 years before she took early retirement. We moved to a golf community in West Palm Beach, FL, in 2000 and live there still.

With time to take care of myself and with the use of a new therapy, I have been able to lead a fairly active life for many more years. My wife and I have been very active in the Alpha-1 Foundation, located in Miami, which for 20 years has financed the research to find a cure for this condition, and to take care of those individuals affected by Alpha-1. I am presently Chairman of the Board of the Foundation.

What led you to UNC and specifically the Chemistry department?

I graduated from Williston Academy in Massachusetts in 1963 and chose UNC because I realized it was an excellent state university. I was led to apply there because my father had done business with a small hardware store in North Carolina called Lowes and had learned about the school first hand from individuals in the business. When we visited the school for an interview I was duly impressed; who wouldn’t be?! What a great place. And that’s only the outside. As soon as you go there as a student, there is so much more on the inside.

I chose Chemistry as a major because I loved science. I grew up in the-era of Sputnik and the space race. As a youngster, along with my brother and others in the Rocket Club, we built and launched rockets in the school athletic fields. I built and flew model airplanes, and developed science projects which grew bigger and more complicated as I grew older. My favorite magazines were Popular Science, Popular Mechanics and Popular Electronics. I wanted to work with my hands as well as my mind to create something new or better. Analytical chemistry, especially working with instruments, sparked my interest immediately, combining chemistry with tools to solve problems and provide the chemists with a means to determine the products and efficiency of their processes.

What inspires you to give to the Chemistry department, and why did you choose to include Carolina chemistry in your will?

UNC was a second step, after Williston, toward deciding what I would do in my career. The inspiration to pursue a higher degree after my time in the service came from remembering that I enjoyed my science classes as an undergraduate and should try to work in a field which was exciting and challenging. I owe UNC a lot! UNC nurtured my interest in science and played a direct role in guiding me to pursue a Ph.D. in Chemistry at UMASS after my service in the Army. The professors at UNC provided me with the stepping stone to a good career working for two great companies in the chemical industry.

As for giving back, generosity, sharing ones good fortune with others, was instilled in me by both my father and mother. My father started from nothing and became a highly successful investment banker. He gave his time, energy and financial guidance back to Brown, his University, as well as many other institutions. My mother would encourage me to always give something to my schools and universities and often do it for me if she thought I was unlikely to do it, for example during my service years.

UNC has been in my estate plan for many years. Recently, Kiley McGrady from the Arts and Sciences Foundation has been visiting me, updating me on progress in Chemistry at UNC and encouraged me to designate my estate gift directly to the Chemistry Department. I believe that emphasis in STEM programs at schools and universities is essential for our future. The world is full of complex issues. Many of these will be solved by the highly educated science-oriented individuals coming out of our universities.

For questions about stock or estate gifts, gifts of cash, and many other means of giving as well as suggestions on how you can support Carolina Chemistry, please contact:

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measurements eliminate the ambiguities present in ensembles, which Chapel Hill Analytical and Nanofabrication Laboratory, CHANL. These fabrication performed with the tools and cleanrooms available in the Such measurements are tricky and often require complex steps of to probe the physical properties of the materials, the Cahoon group

Advancements in semiconductors are a driving force behind many of the technologies we use today, from the smartphones in our pocket, to TVs on our walls, and the solar cells on our rooftops. The Cahoon group focuses on the "bottom-up" chemical synthesis of semiconductor materials that are nanoscale in size. A typical material will have features measuring several nanometers in length, a scale about 10,000 times smaller than the width of a human hair. On this length scale, the materials develop physical properties that strongly depend on size, shape, and composition, enabling a range of potential technologies.

Semiconductor technology has typically been developed using top-down fabrication techniques that pattern semiconductors on increasingly short length scales. For instance, advancements in photolithography, a top-down technique in which light is used to pattern semiconductors such as silicon, have been a driving force behind the ever-decreasing size, cost, and increasing speed of computers. However, this technology has begun to reach fundamental limits. One central project in the Cahoon group is to explore methods to chemically synthesize silicon and encode the same type of complex patterns that would typically be created by lithography, but on potentially shorter length scales.

Silicon "nanowires," cylindrical single-crystals with diameters in the nanometer regime, are grown using a nanoscale metal catalyst by a process termed vapor-liquid-solid, VLS, growth. Semiconductor material is transported in the vapor phase to a liquid catalyst, growing a one-dimensional solid nanowire. By changing the materials supplied in the vapor phase, the composition of the wire can be altered during its growth. This strategy means that "encoded time" directly corresponds to "encoded length" in the wire. By continuously changing composition, the wire has a nanoscale "bar code" of information encoded in its chemical composition. Research in the Cahoon group has shown that this bar code of chemical information can be changed on length scales less than 5 nanometers, a scale that is competitive with or better than the most advanced lithography systems.

When the wire growth process is finished, the wires are etched in solution to reveal the bar code. The process produces wires with complex shapes and is nicknamed ENGRAVE, Encoded Nanowire GRowth and Appearance through VLS and Etching. With a well-developed method to engrave nanowires, one of the Lego building blocks, the Cahoon group has focused on the physical properties encoded by composition and shape. For instance, the group is actively probing how shape affects the absorption and scattering of light at wavelengths that are much longer than the typical size of the wires. The complex interactions of these structures with light are expected to have applications in photovoltaics and solar energy. In addition, the Cahoon group is probing how shape can be used to control the transport of electrons. In one application, a constriction in the wire was used to reversibly stop the flow of electrons, providing the basis for non-volatile computer memory.

To probe the physical properties of the materials, the Cahoon group often performs measurements on single nanoscale semiconductors. Such measurements are tricky and often require complex steps of fabrication performed with the tools and cleanrooms available in the Chapel Hill Analytical and Nanofabrication Laboratory, CHANL. These measurements eliminate the ambiguities present in ensembles, which would average over many different structures. In addition, the Cahoon group collaborates with the Papanikolas group to measure the ultrafast dynamics of single nanowires. Using a pump-probe microscope developed in the Papanikolas group, the time-resolved dynamics in single wires, including the motion of electrons and motion of thermal energy, can be directly visualized. These types of measurements provide a direct probe of the physical properties the materials, resolving questions about the complex connection between composition, shape, and properties in nanomaterials.

Moving away from silicon, a related project in the Cahoon group focuses on the design of materials for solar fuels. As a part of the UNC Energy Frontier Research Center, EFRC, the group is developing semiconductors that enable the efficient conversion of sunlight into solar fuels, which are chemicals that store energy from sunlight in chemical bonds. Nanoscale semiconductors with high surface areas, in conjunction with light-absorbing and catalytic molecules developed within the EFRC, are needed to develop these devices. For instance, the Cahoon group has designed two-dimensional platelets of nickel oxide that are only a few nanometers thick but hundreds of nanometers in width. Because it is so thin, this material retains a high surface area yet can efficiently transport electrons in the other two dimensions. The rational design of materials for solar fuels, by controlling both composition and morphology, is a continuing effort both within the Cahoon group and the EFRC.

Semiconductor nanomaterials provide a rich platform for the development of materials with specific properties and functions. The Cahoon group strives to maintain an approach to science that forefronts creative use of nanoscale materials as the building blocks for the next generation of optic, electronic, and solar technologies.

The Cahoon Group The Physical Chemistry of Nano

If you have ever had the opportunity to watch a child, or an adult, that matter created by Lego building blocks, you know that the manipulative manner of these building blocks allows for a wide range of creative assembly options. If you ask the child about their reasoning for choosing specific structures, they will likely explain both the form and the function of their work, detailing their interest and the need for such a structure. Though researchers in the Cahoon group are not building spaceships, submarines, or racing cars, yet, they are pursuing a similar creative and practical task, except their building blocks are nanoscale semiconductors and the desired functions are in the areas of optics, electronics, and solar energy.
A complex structure quickly emerges from the liquid resin in a Carbon3D printer
Morehead Laboratories: A Chemistry Engine

At the University of North Carolina at Chapel Hill, the Department of Chemistry is the sole provider of many of these required courses, designed to provide chemical laboratory proficiency. Morehead Laboratories, completed in 1986, houses our Undergraduate Lab Program in Chemistry. For almost thirty years, every chemist, biochemist, environmental scientist, nurse, medical practitioner, dentist, dental assistant, biologist, pharmacist, et cetera, graduating from UNC, have passed through our labs. This year, we served over 5100 undergraduate students, offering eleven different lab courses during the academic year.

We have seen a steady increase in enrollment over the last eleven years in virtually all undergraduate chemistry courses. This includes our lab courses. From 2005, the annual enrollment in all undergraduate lab courses has increased by 29%, from just under 4000 to over 5100 students. While other buildings have been added to the Science Complex during this time, our lab space has not increased, and we are nearing physical space capacity in Morehead Laboratories.

Our undergraduates gain hands-on experience with a variety of modern instrumentation, including two recent upgrades. For the introductory analytical lab course, new PASCO wireless spectrometers are being used to analyze the separation of pigments in spinach. The students prepare an extract of the spinach that is run through a liquid chromatography column and monitor its light absorption over time. A new Nanalysis 60 MHz benchtop NMR was acquired for organic chemistry labs. Students prepare and run their own samples and use proton NMR data to identify unknown compounds and confirm their products.

Beginning in the summer of 2014, renovations of the upper-level lab rooms began. To date, six teaching labs have been renovated with new student hoods and lighting, and the remaining two rooms are scheduled to be completed before the next academic year. Additional infrastructure projects are in the planning stages.

Improvements are being implemented to make the labs more sustainable. Green chemistry experiments have been added into the curriculum for inorganic and organic chemistry lab courses. Procedures have been revised to reduce and/or eliminate hazardous waste. We are piloting a program to recycle gloves. Additional proposals are being explored to make our labs greener.

Mark Koza, Kathleen Nevins, Lori Del Negro, and Nita Eskew

Photoredox Catalysis

An organic photoredox-based catalyst system, consisting of an acridinium photocoxidant and a nitroxy radical, promotes site-selective amination of a variety of simple and complex aromatics with heteroaromatic azoles of interest in pharmaceutical research.

The group members also describe the atom-economical use of ammonia to form anilines, without the need for prefunctionalization of the aromatic component. The mildness of this protocol makes it appealing for a variety of applications. Moreover, the group anticipates that this general method for the activation of arenes will result in the development of additional transformations.

Allbritton in NAI

The National Academy of Inventors has named Kenan Distinguished Professor of Chemistry Nancy Allbritton, an NAI Fellow.

Allbritton invented analytical techniques with accompanying instrumentation to perform single-cell biochemical assays for both biomedical research and clinical diagnostics. She also pioneered a new strategy to separate single cells using arrayed-based platforms.
The Lockett Lab Developing 3D Human Tissue Models

Biological systems, even one as straightforward as a small molecule substrate binding to the active site of an enzyme, are elegantly complex. To tease apart the molecular mechanisms driving these systems, we need new tools and models. Tools are nominally the assays, methods, and instrumentation, that allow us to quantify a component of the system accurately. Models are simplified, yet representative, versions of the biological system of interest, which, if experimentally well defined, allow us to tackle tractable questions. Biochemistry is rich in models, ranging from lambda DNA and carbonic anhydrase, to E. coli and C. elegans, all of which provide an experimental framework for the study of various phenomena. These models are successful because they are readily accessible, have an evolving set of tools, and allow probing with different analytical modalities, at different resolutions, and from different experimental perspectives.

In the Lockett Group, we are actively studying cellular responses to gradients of small molecules such as oxygen, glucose, and hydronium ions, pH, in the extracellular matrix. We also study the role of lipid structure and composition in tuning the stability and catalytic activity of membrane-associated metalloenzymes, and the role of the protein scaffold in tuning the redox potential of the metal centers they surround in these metalloenzymes. Each of these somewhat disparate topics aims to develop new models and tools to specifically address the importance of the “chemical environment” in shaping the behavior of biomolecules, biomolecular assemblies, and cells.

One of these models is a three-dimensional, 3D, culture system in which we generate tissue-like environments, representative of a solid tumor. Cellular phenotypes in 3D cultures are more representative of human tissue than the current experimental mainstay, a monolayer of cells on a flat surface. These differences can be attributed to the limited number of cell-cell and cell-extracellular matrix interactions that form between cells in a monolayer. Monolayer cultures are also exposed to a constant supply of nutrients, and cannot mimic the gradients of nutrients and waste products that form in the diffusion-dominated environment of a solid tumor. The steepness and shape of these gradients, which result from cellular proliferation outpacing blood vessel formation, are dynamic and responsible for shaping the abnormal phenotypes associated with tumorigenic cells.

We are developing an alternative tissue model that uses paper-based scaffolds to culture cells. Paper is ubiquitous in the laboratory, is readily patterned with commercial printers and can be cut into desired shapes with scissors. Paper is also three-dimensional by nature, defined by the thickness of the sheet, and offers a simple material for maintaining the thickness of the sheet, and offers a simple material for maintaining cellular movement and phenotypes based on their location in the culture.

We generate oxygen gradients in our tissue model, and experimentally probe the relationship between cellular phenotype and invasiveness in environments of decreased oxygen tension. In particular, we are developing tools to specifically quantify the shape and steepness of the gradients formed in our cultures. We then measure oxygen consumption at different oxygen tensions, evaluate changes in cellular phenotype and invasiveness as a function of oxygen tension, and determine the chemo-sensitivity of the populations of cells in the culture undergoing different oxygen stresses. With this model, we have recently shown that oxygen, in addition to modulating cellular phenotype, is a chemoattractant and directs cellular movement to regions of higher oxygen tension.

Our protein-centric efforts also aim to develop models that are accessible to many laboratories, and experimentally probe the effect of the chemical environment on the function of metalloenzymes. One effort is to develop an automated assembly line approach of preparing cytochrome P450 enzymes, which are membrane-bound and notoriously difficult to express and purify. We envision a system where one merely controls the inputs, such as a gene of interest, lipids of interest, cofactors, et cetera, to obtain functional enzymes in a defined lipid environment. To achieve this goal, we use microfluidic-based technologies that can easily manipulate small volumes of liquid and are capable of generating droplet micro-reactors. Many tools are needed to accurately quantify the protein and lipid compositions of these droplets, and evaluate their activity.

In another effort, we are developing chemistries to immobilize the metal iron-iron center of hydrogenase on carbon electrodes. These surfaces represent a chemical sandbox in which we can easily introduce molecules to the surface and build protein-like shells around the metal centers. Hydrogenase is an interesting model because it interconverts protons and H₂ gas under extremely favorable conditions, approximately –0.4 V versus a standard hydrogen electrode. When the protein scaffold is removed, the iron-iron center maintains functionality but at a greatly decreased favorability. This change in redox potential raises an important question, what exactly is the protein shell doing to protect the metal iron-iron center? We generate oxygen gradients in our tissue model, and experimentally probe the relationship between cellular phenotype and invasiveness in environments of decreased oxygen tension. In particular, we are developing tools to specifically quantify the shape and steepness of the gradients formed in our cultures. We then measure oxygen consumption at different oxygen tensions, evaluate changes in cellular phenotype and invasiveness as a function of oxygen tension, and determine the chemo-sensitivity of the populations of cells in the culture undergoing different oxygen stresses. With this model, we have recently shown that oxygen, in addition to modulating cellular phenotype, is a chemoattractant and directs cellular movement to regions of higher oxygen tension.

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Support Chemistry!

The “Say Yes” fund in Chemistry allows our Department Chair to say “YES” to special and often urgent requests from faculty and students. These small amounts of support, contribute greatly to their research and education.

A gift of any size will make a tremendous difference in our ability to support our outstanding faculty and students.

Please give online!
www.chem.unc.edu/give/

Your continued support is greatly appreciated.

Joseph Templeton to London

The spring semester of 2016 will find Joe and Claudia Templeton watching over twenty-some undergraduates who are tackling the London Honors Program. With multiple courses to choose from and an internship that requires twenty hours a week, our students will be busy, busy, busy. Joe and Claudia took students to London back in 1999 so this will be a reprise; rather like the repeat period Joe had as Interim Chair these past few months. “Not many of us get a second chance, but this academic year 2015-2016 is filled with second chances for me, a real luxury,” comments Joe.

The London Honors Program is housed in Winston House, the London location for UNC activities with students studying abroad. It is located on Bedford Square just behind the British Museum. Students choose from a menu of courses, and the list for the spring semester is shown below. “Looks pretty good, doesn’t it,” says Joe with a smile. His responsibilities will be to keep track of all of the students at all times and to teach two of the courses below. “No, I am not telling which ones,” says Joe with an even broader smile.

- Group Theories: Comparing the Cultures
- The London Art World
- Journalism and Society
- Contemporary British Politics
- Imagining Literary London
- Contemporary London Theatre and its Origins
- The London Experience
- Internship

Harvey Clayton Alumni Visit

Reverend Harvey M. Clayton graduated with a Bachelor of Science in Chemistry from the department in 1965, and we were fortunate to meet him at his 50th class reunion this summer. After graduating, Harvey spent two years with the Peace Corps in Ghana, West Africa, teaching basic chemistry. “My time in Ghana became the most formative single experience of my life,” says Harvey. His experiences there produced a lasting love for the country and its people, and a strong conviction that racial, ethnic, social, economic, and religious differences among people are a richness to be explored and appreciated, rather than differences to be feared. Harvey still hopes to go back one day.

After returning to The United States, Harvey continued to teach chemistry, then served thirty-four years as an analytical chemist with the North Carolina Department of Agriculture and Consumer Services in Raleigh. While still working, Harvey went to the then newly opened School of Divinity at Campbell University in Buies Creek, from where he graduated with distinction with a Master of Divinity in 2005. Ordained as a Baptist minister in 2006, he then served two rural churches as Interim Pastor, and volunteered as an on-call Chaplain for a local hospital. Currently, having completed a first-level certification with the International Conference of Police Chaplains, Harvey volunteers as one of three chaplains for a local police department.

Harvey is firm believer in continuing education, a voracious reader, and his visit to the department was a very enjoyable experience for everybody. Please contact us if you too want to share your memories and come for a visit!
In this issue:

Morehead Laboratories
Aloha, Valerie Ashby
The Cahoon Group
DeSimone on 3D Printing
The Lockett Group