NASC: Bringing Together Supramolecular Chemists From Across North America

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Early-career scientists need opportunities to present their research and to network. Within the supramolecular chemistry community, local conferences that provide such opportunities have arisen over the last few decades. However, a suitable conference in North America was still missing. In 2022, we therefore organized the first North American Supramolecular Chemistry (NASC) meeting to bring together supramolecular chemists from across the continent and to provide career building opportunities for PhD students and postdocs. For this Conference Proceeding, we asked some of the invited speakers, as well as the winners of the best talk prizes, to provide their opinion of the meeting and their vision on the future of supramolecular chemistry in North America.

Introduction from the organizer (Nathalie Busschaert)

Since its inception in the 1960's and 70's supramolecular chemistry has evolved from a purely academic subject studying the interactions between molecules, to a mature field that has found applications in medicine, materials science, catalysis, and other research fields and industries. As a result, there are now many research groups across the world that identify fully or partially as supramolecular chemists. This has created a need for conferences and meetings that can bring together supramolecular chemists on a regular basis, in order to encourage collaboration, inspire new ideas and foster the new generation. International conferences (such as ISMSC) fill part of this void, but offer little opportunities for PhD students, postdoctoral researchers, and other early-career researchers to present their research and improve their network. Local conferences are more suited for this purpose, as they can create a strong local community and provide more flexibility in scheduling early-career researchers. By providing opportunities for PhD students and postdocs to disseminate their research, we can enhance their career prospects and ensure the future of the field. Such local supramolecular chemistry conferences have emerged all over the world (e.g., MASC in the United Kingdom, and SupraChem in Germany), but a suitable local conference in North America was still missing. Hence, the idea of a North American Supramolecular Chemistry (NASC) meeting was born.

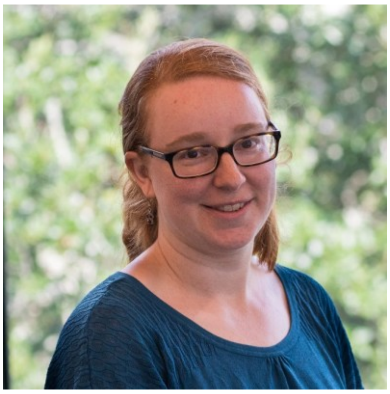

Figure 1. Nathalie Busschaert. Chair and founder of the North American Supramolecular Chemistry (NASC) meeting. Assistant Professor at Tulane University.

The first NASC meeting was held in New Orleans on December 19-20, 2022. The meeting involved seminars by 2 keynote speakers, 9 invited speakers and 17 flash talk presenters that were selected from 35 submitted abstracts; providing an approximate 60-40 ratio in favor of early-career scientists. In addition, the first night also included a poster session and banquet to encourage [scientific] discussion and networking. With 88 registered attendants, we considered the meeting a successful first edition and it clearly showed the demand for this type of conference in the North American supramolecular chemistry community. The meeting covered all the best supramolecular chemistry has to offer, ranging from fundamental science studying lesser-known intermolecular interactions (e.g., chalcogen bonding, pnictogen bonding, and n→π* interactions) to more application-driven research (e.g., MOFs, materials science, medical applications, sensing, molecular switches and molecular machines), and finished with capturing career advice and life lessons from Nobel Laureate Fraser

Stoddart. For this Conference Proceeding, we asked some of the invited speakers, as well as the winners of the best talk prizes, to provide their opinion of the meeting and their vision on the future of supramolecular chemistry in North America.

Impressions of NASC-2022 speakers

Shining light on (Supra)molecular systems: artificial molecular machines and photoactive cages (Víctor García-López)

The first North American Supramolecular (NASC) meeting was a fantastic conference whose format and cost allowed broad participation, reflecting the community's welcoming and supportive atmosphere. Notably, the meeting offered a unique opportunity for students and postdocs to showcase their research through talks and poster presentations. Thus, it was thrilling to see the enthusiasm of young scientists and their level of engagement with other students and senior researchers. Moreover, the meeting fostered a unique environment by bringing together scientists from different subfields, enabling new collaborations, and stimulating discussions essential to push the boundaries of supramolecular chemistry and delivering the next generation of materials, therapies, and sensors. In that regard, the field of artificial molecular machines will significantly influence the broader fields of biology and catalysis in the coming years. Already, molecular machines have provided new paradigms to kill cancer cells by disrupting the cell membrane, facilitating the delivery of antibiotics to drug-resistant bacteria, modulating ion transport across membranes, and as tools to interrogate cells and study mechanotransduction. Although such examples are at the proof-of-concept stage, multidisciplinary collaborations will tackle critical fundamental challenges to eventually develop fully biocompatible synthetic machines activated by light- or cellgenerated stimuli and whose collective action results in a well-regulated biological response. In catalysis, molecular machines could provide new multi-responsive systems whose mechanical motion and dynamics control molecular recognition and chemical reactivity with high stereoselectivity. Moreover, understanding and harnessing the effect of nanoconfinement and compartmentalization in electron and energy transfer processes will unlock a new generation of photocatalysts. Thus, molecular containers, such as cages, capsules, and cavitands, decorated with photosensitizers in their framework will enable new concepts in synthetic photochemistry.

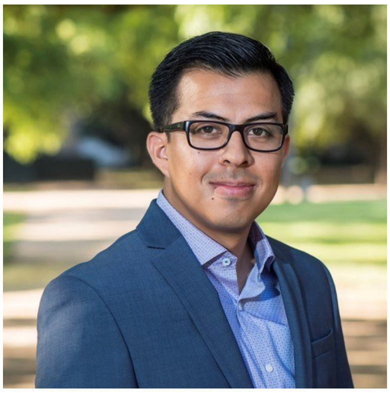

Figure 2. Víctor García-López. Invited speaker at NASC-2022. Assistant Professor at Louisiana State University.

Supramolecularly designed materials for sustainability (Chenfeng Ke)

Integrating supramolecular designs into the development of functional materials enabled the discovery of new-generation materials with better performance, longer life spans, and better recyclability. Supramolecular binding motifs form dynamic and reversible structures and superstructures across the nano-to-macroscale, providing unique opportunities to tackle emerging sustainability challenges, such as water pollution and plastic recycling. For example, porous frameworks featuring supramolecular designed architectures (e.g. hydrogen-bonded crosslinked organic frameworks) have been introduced as sorbents for water purification and sensors to detect harmful chemicals. The ability to dynamically control these supramolecular framework materials' structure and properties allows for selectively removing stable chemical pollutants in water. Furthermore, when non-covalent binding moieties are introduced to traditional polymer networks, the supramolecularly designed polymers positively impact sustainability because they can be designed to self-heal, reducing the need for replacement and repairs. An exciting application is using them for 3D printing to create complex and functional soft materials. These materials could be fabricated in various geometries while being flexible and responsive to external stimuli, which are not attainable with traditional 3D printing materials.

Figure 3. Chenfeng Ke. Invited speaker at NASC-2022. Associate Professor at Dartmouth College.

Sigma-hole bonding: functional materials and synthetic biology (C. Michael McGuirk)

In the late 1990's and early 2000's, contemporaneous computational efforts by Politzer and Murray and empirical efforts by Resnati and Metrangolo resulted in an effective rediscovery of halogen bonding and introduction of the concept of sigma-hole bonding.

Since then, the supramolecular community has undergone an explosion of effort to not only understand the electronic origins and structural variables of these noncovalent interactions, but also leverage this knowledge to effectively use halogen bonding in cornerstone supramolecular applications of crystal engineering, sensing, molecular machines, and catalysis, often directly in place of hydrogen bonding. With the success of understanding and applying halogen bonding, the supramolecular community pushed back into the periodic table, recognizing that just as hydrogen bonding is not wholly unique neither is halogen bonding. Indeed, weakly electronegative chalcogens, pnictogens, and tetrels can form analogous noncovalent interactions, all under the umbrella of sigma-hole bonding. While not there yet, efforts to re-create what has been accomplished with halogen bonding with chalcogen, pnictogen, and tetrel bonding have undergone a significant recent uptick. *So, then, what is the future of sigma-hole bonding?* Perhaps the greatest long-term opportunities are in the study and application of these interactions in areas that aren't classically considered in the realm of supramolecular chemistry, but at their core, surely are. For example, hydrogen bonding has emerged as a powerful tool in the assembly and stabilization of permanently porous framework materials, giving rise to a complementary family of functional materials to covalent and coordination (i.e., metal–organic) based frameworks. Owing to the relatively high directionality of sigma-hole bonding interactions, relative to hydrogen boning, and the varying levels of valency of sigma-hole bond donors, such interactions may serve as a conceptual intermediate between hydrogen bonding and coordination for framework assembly. While also producing materials with unexpected aggregates of physical and functional properties. Synthetic biology presents an almost overwhelming amount of possibility for sigma-hole bonding. One only needs to consider the immense roles of hydrogen bonding in the structures and functions of proteins, DNA, and RNA.

With the catalog of donor species, structures, and valencies, the realization of bio-compatible synthetic amino acids or nucleobases containing sigma-hole bonding donor/acceptor species presents an unexplored path to designer proteins and expanding data storage in DNA.

It is indeed an exciting time in the world of sigma-hole bonding. But, to keep the field from stagnating the in near future, we must look beyond the archetypal subfields of supramolecular chemistry, seeking opportunities where the subtle uniqueness of sigma-hole donors can actualize functional differences in materials and synthetic biology.

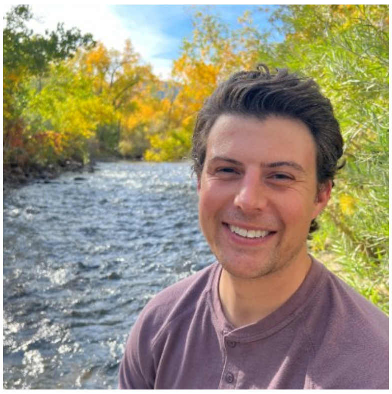

Figure 4. C. Michael McGuirk. Invited speaker at NASC-2022. Assistant Professor at Colorado School of Mines.

Precise supramolecular containers for modulating reactions (Linda S. Shimizu)

While the supramolecular toolbox is employed by many types of chemical and biological researchers, the NASC meeting afforded a refreshing opportunity for supramolecular chemists to network and share their latest results in a more focused setting. It is indeed an exciting time to engage in the design of supramolecular systems, as computational methods and machine learning offer new ways to analyze experimental results and predict properties. Supramolecular interactions and strategies play a crucial role in modern methodology and have improved yields in macrocyclizations through templation, catalyst design, and dynamic covalent methods. Our research focuses on dimerizations, electron transfer reactions, and polymerizations in nanochannels of self-assembled bis-urea macrocycles. The wider community has employed confined nanospaces of supramolecular capsules, which are typically dimeric, as well as larger channels and spaces within assemblies, micelles, coordination polymers and crystals to modulate product distributions, enhance conversion, employ safer reagents, stabilize reactive intermediates, and modulate regio- and stereoselectivity of reactions. Such nanoreactors also offer opportunities to probe mechanisms in controlled environments. Control over the topology and size of supramolecular assemblies and their polymeric counterparts open a creative space to push the envelope of these methods. Potentially this would enable precise synthesis of new materials at predictable lengths scales, from the molecular to the polymeric range (1-50 nm), to systematically study effects of size and organization on physical properties and chemical reactions.

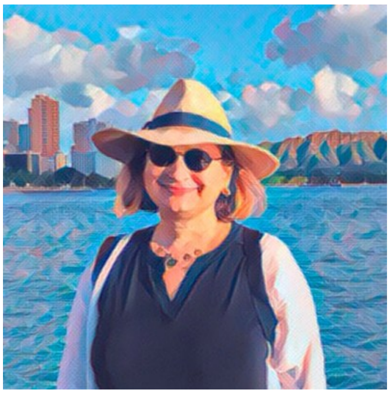

Figure 5. Linda S. Shimizu. Invited speaker at NASC-2022. Professor at the University of South Carolina .

Supramolecular chemistry to expand materials discovery (Margaret C. Gerthoffer)

Chemistry is often divided into five main subfields: physical, organic, inorganic, analytical, and biochemistry. Yet, chemical innovation spans widely into multimodal world applications through the derivation of new materials, medicine, food chemistry, biochemical pathway elucidation, and more. The pursuit of fundamental research often requires a cross-section of knowledge, skills, and techniques to harbor innovation. Supramolecular chemistry is, most simply, the study of intermolecular interactions, which, as highlighted from the presentations at NASC, sits at the forefront of importance within all major chemistry fields. These highly directional interactions interplay within solid-state reactions to form polymers has been studied by my research group to design and guide the formation of a new form of carbon allotrope, the diamond nanothread.

This allotrope is considered a thread of diamond due to its sp^3 character and incredibly thin architecture. Nanothreads are formed through the solid-state compression of primarily simple aromatics (*i.e.,* benzene) through concurrent cycloadditions that occur in one direction to form a six-carbon atom core at 10s of GPa. A key challenge of nanothread formation is that the synthesis proceeds through monomers that favor spontaneous reactions under pressure to form amorphous carbon rather than crystalline threads. Supramolecular chemistry offers a method to control the solid-state reactivity to proceed in one uniform direction using co-crystals to yield a crystalline product. To date, our group dictated precise intermolecular interactions in closely eclipsed π-stacked monomers to collapse into one-dimensional nanothreads by design. The development of nanothreads has thus relied on employing supramolecular chemistry to understand how to purposefully design application-specific high-tensile strength materials. With the necessary intersection and development of more niche fields of research, applying the principles of supramolecular chemistry is necessary for exploring new materials.

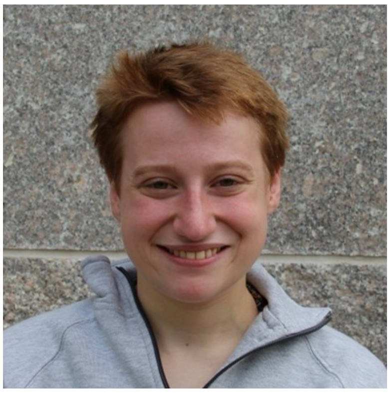

Figure 6. Margaret C. Gerthoffer. Flash talk presenter at NASC-2022 and winner of the 'best talk' prize. PhD student in the group of Elizabeth Elacqua at the Pennsylvania State University.

In-person conferences facilitate professional development in a post-pandemic world (Nabarupa Bhattacharjee)

Supramolecular chemistry currently transcends the space of simple host-guest chemistry. The field has now evolved to shelter a variety of interdisciplinary research goals interfacing with materials and biological chemistry. In addition to independent strides, advancement of the field is bound to benefit from scientific interactions. These can help expand our knowledge about current research in the field and promote fruitful collaborations so that we can collectively contribute to address global challenges. The last two years have been extremely taxing for scientists around the globe and especially for graduate students delaying their professional development. A major part of graduate education involves honing skills to be able to present one's research lucidly in front of a broader audience. Virtual meetings during the pandemic have proved extremely crucial in gluing together researchers around the world, nevertheless opportunities for personal communication with like-minded scientists in the field is incomparable. Intergenerational conversations between graduate students, postdocs and established professors in the field are often key to the development of newer ideas and directions in research. Moreover, for in-person conferences, positive reinforcements in the form of appreciation of research work through prizes also helps inculcate motivation. Therein, field-specific conferences like the North American Supramolecular Chemistry meeting (NASC 2022) have taken the much-needed step in actively keeping alive the essence of the breadth and depth of macrocyclic and supramolecular chemistry. The efforts made by the organizers to bring supramolecular chemists from around North America together and facilitate networking opportunities among scientists needs to be commended. The inaugural NASC meeting provided the center stage for a significant number of graduate students and postdocs to present their research. Success of these events will help guide conference organizers on how to plan future meetings in a post-pandemic world.

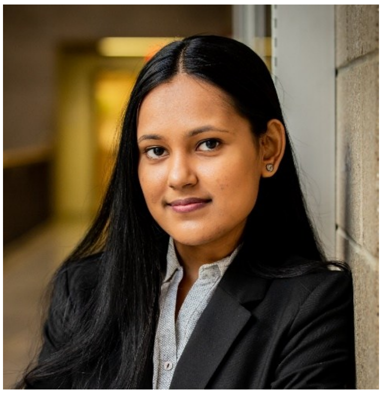

Figure 7. Nabarupa Bhattacharjee. Flash talk presenter at NASC-2022 and runner-up of the ‘best talk’ prize. PhD student in the group of Amar Flood at the University of Indiana, Bloomington.

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Disclosure statement

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