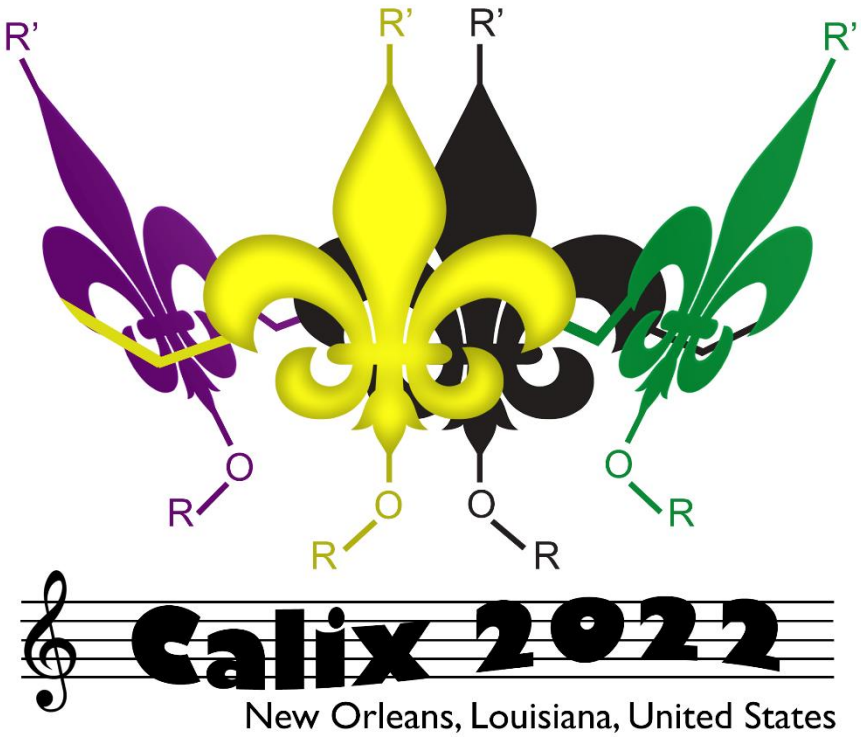


16th International Conference on Calixarenes

Program & Book of Abstracts

July 10 – July 14, 2022
New Orleans, USA

FOREWORD

On behalf of the organizing committee, it is our pleasure to welcome you to New Orleans, the Monteleone Hotel, and the **16th International Conference on Calixarenes (Calix 2022)**. Calix 2022 aims to bring together academic and industrial attendees from around the globe to discuss all aspects of calixarenes and related macrocyclic compounds. It will also offer networking opportunities among recognized leaders in the field, young scientists, and students. In addition, there will be a reflective workshop organized by Women in Supramolecular Chemistry (WISC) to offer all participants (men and women) the opportunity to creatively reflect on their research, their career path, and other aspects of academic life.

This book contains the abstracts of the fourth C. David Gutsche Award lecture by Professor Javier De Mendoza, 6 plenary lectures, 22 invited lectures, 17 contributing lectures, 4 flash presentations and ~25 posters presented at the 16th International Conference on Calixarenes.

Beyond the scientific program, please find time to enjoy the vibrant southern US city of New Orleans. The famous Hotel Monteleone, located in the heart of the historic French Quarter, is the ideal basecamp for attendees to explore New Orleans' unique culture of festivals, music and Creole/Cajun cuisine. Laissez les bons temps rouler! (Let the good time roll!)

Code of conduct - To work towards the betterment of society, all organizations must be diverse, equitable, and inclusive; they must each be communities that welcome and support a diverse array of peoples. At Calix 2022 we believe we must foster an environment where each member of our academic and industrial family, particularly our Black, Indigenous, and People of Color and other underrepresented members, are not only supported, but are able to thrive. Over the past several years, the Calix Symposium Series has made great progress in this regard, but we know we can always do more. So please join us at Calix 2022 in identifying and removing the systematic barriers that have barred marginalized communities from full participation in the scientific community.

Yours sincerely,
The local organizing committee

The local organizing committee

Nathalie Busschaert (Tulane University, USA)
Bruce Gibb (Tulane University, USA)
Corinne Gibb (Tulane University, USA)
Janarthanan Jayawickramarajah (Tulane University, USA)
Jonathan Sessler (University of Texas at Austin, USA)
Richard Hooley (University of California at Riverside, USA)

The international advisory committee

Europe, Middle-East, and Africa

Alessandro Casnati (University of Parma, Italy)
Michaele Hardie (University of Leeds, UK)
Olivia Reinaud (University Paris Descartes, France)

Asia-Pacific

Mei-Xiang Wang (Tsinghua University, China)
Jong Seung Kim (Korea University, South Korea)
Tomoki Ogoshi (Kyoto University, Japan)

Americas

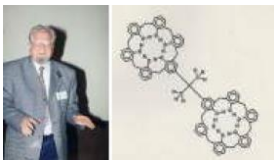
Bruce Gibb (Tulane University, USA)
Jonathan Sessler (University of Texas at Austin, USA)
Fraser Hof (University of Victoria, Canada)

Honorary Member(s)

Olivier Siri (Aix Marseille Univ., France)

HISTORY OF THE INTERNATIONAL CONFERENCE ON CALIXARENES

1991: Workshop on Calixarenes and Related Compounds
Location: Mainz (Germany)
Organizer: V. Böhmer (Johannes Gutenberg Universität)



1993: Workshop on Calixarenes and Related Compounds
Location: Kurume (Japan)
Organizer: S. Shinkai(Kyushu University)

1995: 3rd International Calixarene Conference
Location: Fort Worth (USA)
Organizer: C. D. Gutsche (Texas Christian University)

1997: 4th International Conference on Calixarenes
Location: Parma (Italy)
Organizers: R. Ungaro and
A. Pochini (Università di Parma)

1999: 5th International Conference on Calixarenes
Location: Perth (Australia)
Organizer: J. Harrowfield (University of Western Australia)

2001: 6th International Conference on Calixarenes
Location: Enschede (Netherlands)
Organizer: D. N. Reinhoudt (University of Twente)

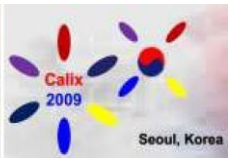
2003: 7th International Conference on Calixarenes
Location: vancouver (Canada)
Organizers: J. Sherman (Univ. of British Columbia) and B. Gibb (Univ. of New Orleans)

2005: 8th International Conference on Calixarenes
Location: Prague (Czech Republic)
Organizers: I. Stibor and P. Lhoták (Prague Institute of Chemical Technology)

2007: 9th International Conference on Calixarenes
Location: Maryland (USA)
Organizer: J. T. Davis (University of Maryland)


2009: 10th International Conference on Calixarenes
Location: Seoul (South Korea)
Organizers: J. S. Kim (Korea University) and
K. Kim (POSTECH)





2011: 11th International Conference on Calixarenes
Location: Tarragona (Spain)
Organizers: J. de Mendoza (ICIQ) and
P. Ballester (ICREA-ICIQ)



2013: 12th International Conference on Calixarenes
Location: St. John's (Canada)
Organizer: P. E. Georghiou (Memorial University of Newfoundland)


2015: 13th International Conference on Calixarenes
Location: Giardini Naxos (Italy)
Organizers: P. Neri (Univ. di Salerno) and
M. Parisi (Univ. di Messina)



2017: 14th International Conference on Calixarenes
Location: Tianjin (China)
Organizer: Y. Liu (Nankai University)


2019: 15th International Conference on Calixarenes
Location: Cassis (France)
Organizer: O. Siri (Aix-Marseille, Univ.),
O. Reinaud (Paris-Descartes Univ.), and
J.-M. Raimondo (Aix-Marseille Univ.)




SPONSORS

Tulane University

Taylor & Francis
Taylor & Francis Group

Supramolecular CHEMISTRY
Edited by Philip A. Gale and Bruce C. Gibb

Tulane University
Department of Chemistry

Sessler Family Charitable Trust

PROGRAM

Sunday July 10th

Reception and Registration

4:00 – 7:00 pm Registration in Monteleone Hotel (Riverview Room, rooftop)
5:00 – 7:00 pm Welcome Reception (Riverview Room, rooftop)

Dinner on own

Monday July 11th

Session 1 (Chair: Kate Joliffe)

8:00 am – Registration and scientific session (Vieux Carré Room)

8:20 – 8:30 am Introduction and Welcome Remarks

8:30 – 9:00 am Jonathan Sessler (University of Texas, Austin): *Virtual Presentation*
P1: *Calixpyrroles: From Ion Recognition to Functionalized Materials*

9:00 – 9:30 am Wei Jiang (South University of Science and Technology of China): *Virtual Presentation*
I1: *Biomimetic Molecular Recognition in Water*

9:30 – 10:00 am Enrico Dalcanale (University of Parma)
I2: *Stimuli Responsive Polymers via Molecular Recognition*

10:00 – 10:30 am Darren Johnson (University of Oregon)
I3: *Main Group Supramolecular Chemistry: Self-Assembly of Cyclophanes, Cages, and Macrocycles*

10:30 – 11:00 am Coffee Break

Session 2 (Chair: Liat Avram-Biton)

11:00 – 11:15 am Laura Baldini (University of Parma)
C1: *A Luminescent Calixarene-Based Molecular Thermometer*

11:15 – 11:30 am Eric Masson (Ohio University)
C2: *Cucurbit[8]uril-Secured Platinum Dimers: Recognition and Applications*

11:30 – 11:45 am Mihail Barboiu (University of Montpellier)
C3: *Pillararene Water Channels – Structural Determinants for Enhanced Filtration Performances in Bilayer and Polymeric Membranes*

11:45 – 12:00 pm Hennie Valkenier (Free University of Brussels)
C4: *Transmembrane Transport of Ions by Calixarene-Based Receptors*

12:00 – 12:30 pm Tomoki Ogoshi (Kyoto University)
I4: *Supramolecular Assemblies and Systems Constructed from Planar-Chiral Pillar[n]arenes*

Lunch

12:30 – 2:00 pm Lunch Break

Session 3 (Chair: Nathalie Busschaert)

2:00 – 3:00 pm Women in Supramolecular Chemistry (WISC): *Virtual Presentation*
P2: *The International Women in Supramolecular Chemistry Network*

3:00 – 3:30 pm Alessandro Casnati (University of Parma): *Virtual Presentation*
I5: *Calixarenes in Bionanotechnology*

3:30 – 4:00 pm Coffee Break

Session 4 (Chair: Enrico Dalcanale)

4:00 – 4:30 pm Olivier Siri (Aix-Marseille University)
I6: *Versatile Aminoazacalixarenes*

4:30 – 5:00 pm Carmine Gaeta (University of Salerno)
I7: *Prismarenes: A Novel, Promising Class of Macrocyclic Host Molecules*

5:00 – 5:30 pm Flash Presentations
F1: Ngong Kodiah Beyeh (Oakland University) – *Ionic Resorcinarenes Target Pyrophosphate and αA66-80 Peptide Related to Cataracts*

F2: Victor García-Lopez (Louisiana State University) – *Stimuli-Responsive Resorcin[4]arene Cavitands: Towards Visible Light-Activated Molecular Grippers*

F3: Subba Reddy Mekapothula (Nottingham Trent University) – *Novel Silica-Bound Supramolecular Chromatographic Stationary Phases*

F4: Chelsea Wilson (University of Victoria) – *Large-Scale, Chromatography-Free Ethoxypillar[6]arene Synthesis*

5:30 – 6:00 pm Julius Rebek Jr. (Scripps Research Institute): *Virtual Presentation*
P3: *Molecules Under Confinement*

Evening

On own

Tuesday July 12th

Session 5 (Chair: Arkadi Vigalok)

8:30 – 9:00 am Olivia Reinaud (University Paris Descartes): *Virtual Presentation*
P4: *A Biomimetic Cavity, a Metal Ion and Water: A Trialogue Full of Surprises!*

9:00 – 9:30 am Dong-Sheng Guo (Nankai University): *Virtual Presentation*
I8: *Hypoxia-Responsive Drug Delivery System Based on Azocalixarenes*

9:30 – 10:00 am Mei-Xiang Wang (Tsinghua University): *Virtual Presentation*
I9: *From Calixarenes to Zigzag Hydrocarbon Nanobelts*

10:00 – 10:30 am Liat Avram-Biton (Weizmann Institute of Science)
I10: *Elucidating Dynamics in Host–Guest Systems: a GEST NMR Approach*

10:30 – 11:00 am Coffee Break

Session 6 (Chair: Richard Hooley)

11:00 – 11:15 am Noémie Elgrishi (Louisiana State University)
C5: *Modulating Electrochemical Activity Through Encapsulation*

11:15 – 11:30 am Yannan Lin (University of Pennsylvania)
C6: *A Protonated Hemicryptophane for Selective Binding of Polar Guests and Anions*

11:30 – 11:45 am Jennifer Hiscock (University of Kent): *Virtual Presentation*
C7: *The Therapeutic Potential of Supramolecular Self-Associating Amphiphiles (SSAs)*

11:45 – 12:00 pm Arkadi Vigalok (Tel Aviv University)
C8: *Fostering Host–Guest Sensing in Fluorescent Calixarene Scaffolds*

Lunch

12:00 – 1:00 pm Lunch Break (boxed lunches provided for excursion)

Afternoon

1:00 pm – 5:00 pm Swamp Excursion

Evening

6:00 – 8:00 pm Poster presentations and mixer (Riverview Room, rooftop)

Wednesday July 13th

Session 7 (Chair: Pablo Ballester)

8:15 – 8:30 am C. David Gutsche Award: Introductory Remarks

8:30 – 9:30 am Javier de Mendoza (ICIQ): C. David Gutsche Presentation
CDG: *From Heterocycles to Calixarenes: A Fascinating and Stimulating 45-Year Journey*

9:30 – 9:45 am De-Xian Wang (ICCAS, Beijing): *Virtual Presentation*
C9: *Oxacalix[2]arene[2]triazine-Based Molecular Hourglass*

9:45 – 10:00 am Pavel Lhoták (UCT Prague)
C10: *Unusual Reactivity of Macrocycles – How to Destroy Calixarenes?*

10:00 – 10:30 am Konrad Tiefenbacher (University of Basel)
I11: *Synthesis and Application of Large and Conformationally Restricted Bowl-Shaped Macrocycles*

10:30 – 11:00 am Coffee Break

Session 8 (Chair: Agnieszka Szumna)

11:00 – 11:15 am Peter Crowley (NUI Galway): *Virtual Presentation*
C11: *Calixarene-Mediated Protein Assembly and Encapsulation*

11:15 – 11:30 am Richard Hooley (University of California, Riverside)
C12: *Biosensing with Water-Soluble Deep Cavitands*

11:30 – 11:45 am Adam Urbach (Trinity University): *Virtual Presentation*
C13: *Minimal Protein Affinity Tags*

11:45 – 12:00 pm Xiaodong "Michael" Shi (University of Southern Florida)
C14: *Design and Synthesis of Cyclic Nucleobase as a New Scaffold for Molecular Recognition and Ion Separation*

12:00 – 12:30 pm Werner Nau (Jacobs University, Bremen)
I12: Activating and Monitoring Membrane Transport with Macrocycles

Lunch

12:30 – 2:00 pm Lunch Break

Session 9 (Chair: Mihail Barboiu)

2:00 – 2:30 pm Lyle Isaacs (University of Maryland, College Park)
I13: *Pillar[n]MaxQ: Synthesis, Molecular Recognition Properties, and In Vivo Sequestration Processes*

2:30 – 3:00 pm Melchiorre Parisi (University of Messina)
I14: *Probing the Self-Assembling Behavior of Tubular Macrocycles*

3:00 – 3:30 pm Jovica Badjić (Ohio State University)
I15: *Molecular Baskets*

3:30 – 4:00 pm Coffee Break

Session 10 (Chair: Konrad Tiefenbacher)

4:00 – 4:30 pm Jong Seung Kim (Korea University)
I16: *Triazole Scaffold Calix[n]arenes*

4:30 – 5:00 pm Pablo Ballester (ICIQ)
I17: *Supramolecular Recognition and Sensing of Creatinine Using Phosphonate Aryl-Extended Calix[4]pyrrole Cavitands*

5:00 – 5:15 pm Nathalie Busschaert (Tulane University)
C15: *Supramolecular Hosts Targeting Bacterial Phospholipids*

5:15 – 5:45 pm Yoram Cohen (Tel Aviv University)
I18: *SAR in the Anti-Biofilm Activity of Cationic Pillararenes and the Use of Pillararene Derivatives as Scaffolds for the Preparation of Supramolecular Boxes*

Evening Banquet

7:00 pm – late Oceana Grill (739 Conti Street, corner of Bourbon and Conti)

Thursday July 14th

Session 11 (Chair: Eric Masson)

8:30 – 9:00 am Kate Joliffe (University of Sydney)
P5: *Novel Molecular Receptors for the Recognition, Sensing and Transport of Anions*

9:00 – 9:30 am Feihe Huang (Zhejiang University): *Virtual Presentation*
I19: *Nonporous Adaptive Crystals (NACs) for Separation and Adsorption*

9:30 – 10:00 am Placido Neri (University of Salerno)
I20: *Catalysis Mediated by Hexameric Capsules*

10:00 – 10:30 am Bradley Smith (University of Notre Dame)
I21: *Solid State Self-Assembly of Organic/Inorganic Hybrids*

10:30 – 11:00 am Coffee Break

Session 12 (Chair: Tomoki Ogoshi)

11:00 – 11:15 am Janarthanan Jayawickramarajah (Tulane University)
C16: *Expanding the Toolbox of Dynamic DNA Chemistry with Macrocyclic Hosts*

11:15 – 11:30 am Semin Lee (Louisiana State University)
C17: *Scalable Synthesis and Applications of Cycloparaphenylene-acetylene Carbon Nano-hoops*

11:30 – 12:00 pm Agnieszka Szumna (Polish Academy of Science)
I22: *Mechanochemistry of Molecular Containers*

12:00 – 12:30 pm Philip Gale (University of Sydney)
P6: *Measuring Anion Binding at Biomembrane Interfaces*

12:30 – 12:40 pm Closing Remarks

Lunch

12:40 – 2:00 pm Lunch Break

C. DAVID GUTSCHE AWARD

C. David Gutsche Award

Professor Javier De Mendoza

Institute of Chemical Research of Catalonia (ICIQ)
Tarragona, Spain

The Advisory Committee of the International Conference on Calixarenes has the distinct pleasure to announce that Javier de Mendoza is the 4th recipient of the C. David Gutsche Award. The C. David Gutsche Award is a biennial, $5,000, award to a senior researcher who has made significant contributions to the field of calixarenes. Javier will present his award lecture at the next International Conference on Calixarenes, in New Orleans, USA July 10-14th 2022.

The Advisory Committee

Alessandro Casnati
(University of Parma)

Mei-Xiang Wang
(Tsinghua University)

Bruce Gibb
(Tulane University)

Michaele Hardie
(University of Leeds)

Jong Seung Kim
(Korea University)

Jonathan Sessler
(University of Texas)

Olivia Reinaud
(University Paris Descartes)

Tomoki Ogoshi
(Kyoto University)

Fraser Hof
(University of Victoria)

Olivier Siri
(Aix-Marseille University)

From Heterocycles to Calixarenes: A Fascinating and Stimulating 45-Year Journey

de Mendoza, J.

The Institute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans 16, 43007-Tarragona (Spain)

E-mail: jmendoza@iciq.es

Nowadays, calixarenes are worldwide recognized among the most useful and versatile building blocks to create molecular complexity. Unlike related bowl-shaped or cylindrical scaffolds (i.e. resorcinarenes, cavitands, pillarenes, cucurbiturils, cyclodextrins, cyclotriveratrylene, or coronarenes, among others), calixarenes simultaneously benefit from different sizes, shapes (conformations), controlled functionalization (at either upper and lower rims) and, most remarkably, a subtle balance between rigidity and flexibility, complexity and synthetic effort, which facilitates the design of novel chemical architectures for recognition, self-assembly, catalysis or material sciences.

As a proud and grateful recipient of the fourth Award honoring the memory of C. David Gutsche, a truly visionary scientist on the future of these fascinating molecules and the father of the area for his pioneer work in their chemistry, following and rationalizing early steps on the condensation products of phenol with aldehydes, I want to dedicate this award lecture to Prof. Pilar Prados and also to many colleagues, co-workers and collaborators who made possible our contributions to the field for more than four decades. Without their inspiration and dedication, none of my contributions would have been possible.

SPEAKER ABSTRACTS

P1 Calixpyrroles: From Ion Recognition to Functionalized Materials

Sessler J.L.

Department of Chemistry, The University of Texas at Austin, 105 E. 24th Street-A5300, Austin, TX 78712-1224 USA.
E-mail: sessler@cm.utexas.edu

This presentation will provide a summary of our recent efforts to create calix[4]pyrroles and related receptors for ion pairs and their incorporation into responsive small molecules and materials. Emphasis has been placed on the development of systems that permit the specific recognition and competitive extraction of hard ions, such as the lithium cation and the hydroxide and carbonate anions. Studies of softer ions, such as the cesium cation, as an ion pair component have also been carried out. Using ion pair recognition, an effort has been made to control structure beyond the first coordination sphere. This has been done by creating systems whose polarity and hence morphology changes as a function of ion recognition, allowing for control over, e.g., micelle formation. Toward this end, responsive polymeric systems that permit the capture of dianions and hydroxide anion have been the subject of attention. Separately, several responsive recognition systems have been prepared with the view to being able to bind and release complex anions that have traditionally proved difficult to capture using synthetic receptors, including halide anion salts of lithium and various hydroxide anion salts. The creation of gels for ion capture will also be presented as appropriate.

This presentation is made possible by the dedicated efforts of numerous students and postdoctoral fellows who will be thanked explicitly during the lecture, as well as collaborations with a number of groups, including those of Profs. Philip A. Gale, Han-Yuan Gong, Qing He, Feihe Huang, Tony James, Jan Jeppesen, Xiaofan Ji, Xiaodong Chi, Niveen Khashab, Jong Seung Kim, Sung Kuk Kim, Dong Sub Kim, Changhee Lee, Bruce A. Moyer, Zachariah A. Page, Jung Su Park, Injae Shin, Pall Thordarson, George Schatz, and Jun-Long Zhang.

Over its lifetime this project has been supported at various points by the US National Science Foundation, the U.S. DOE Office of Basic Energy Sciences, the Petroleum Research Fund of the ACS, the Robert A. Welch Foundation, and KAUST.

References

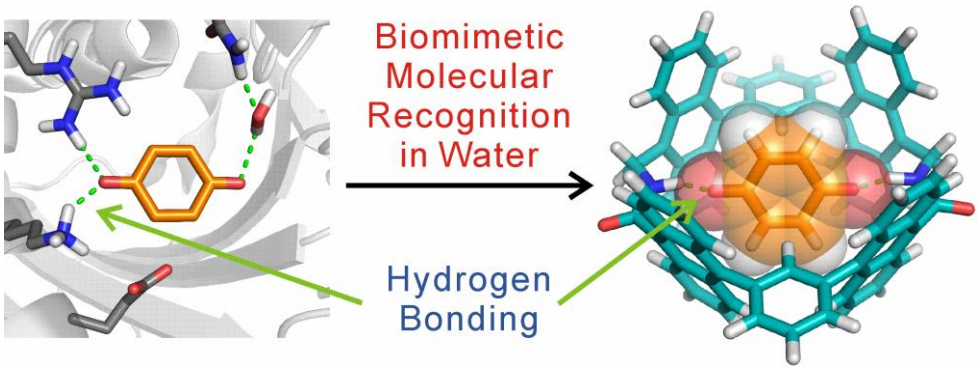
1. T. Hirao, D. S. Kim, X. Chi, V. M. Lynch, K. Ohara, J. S. Park, K. Yamaguchi, J. L. Sessler, *Nature Commun.* **2018**, *9*, 823-831.
2. X. Ji, W. Chen, L. Long, F. Huang, J. L. Sessler, *Chem. Sci.* **2018**, *9*, 7746 - 7752
3. X. Ji, X. Chi, M. Ahmed, L. Long, J. L. Sessler, *Acc. Chem. Res.* **2019**, *52*, 1915-1927.
4. W. Chen, C. Guo, Q. He, X. Chi, V. M. Lynch, Z. Zhang, J. Su, H. Tian, J. L. Sessler, *J. Am. Chem. Soc.* **2019**, *141*, 14798-14806.
5. X. Wang, L. Xie, K. Lin, W. Ma, T. Zhao, X. Ji, N. M. Khashab, M. Alyami, J. L. Sessler, H. Wang, *Angew. Chem. Int. Ed.* **2021**, *60*, 7188-7196.
6. D. Luo, J. Tian, J. L. Sessler, X. Chi, *J. Am. Chem. Soc*. **2021**, *143*, 18849–18853.
7. H. Wang, L. O. Jones, I. Hwang, M. Allen, D. Tao, V. M. Lynch, B. D. Freeman, N. M. Khashab, G. C. Schatz, Z. A. Page, J. L. Sessler, *J. Am. Chem. Soc*. **2021**, *143*, 48, 20403–20410.

I1 Biomimetic Molecular Recognition in Water

Jiang W.

Department of Chemistry, Southern University of Science and Technology, Shenzhen, China.
E-mail: jiangw@sustech.edu.cn

Selective molecular recognition in water is the foundation for catalysis, transportation, bioconjugation, signal transduction and other functions in biological systems. However, it is often challenging for synthetic hosts to differentiate functional organic molecules in water. One of the reasons is that hydrogen bonding cannot be effectively employed in the polar solvent - water. In contrast, bioreceptors realize this through positioning hydrogen bonding sites in a nonpolar microenvironment. By mimicking the binding pocket of bioreceptors, endo-functionalized cavity has been proposed to achieve selective molecular recognition in water. Under this guideline, we have developed a series of water-soluble macrocyclic hosts with an endo-functionalized cavity (for example, amide naphthotubes).[1-4] These hosts are able to selectively recognize a wide variety of functional organic molecules, including drug molecules, small biomolecules, and hydrophilic solvent molecules, in water. In addition, we also found that these hosts or their host-guest complexes can be applied in slide-ring hydrogels,[5] chiroptical sensing of wide-scope substrates,[6,7] noncovalent bioconjugation in living animals,[8] effective removal of polar organic micropollutants from water,[9] and stabilization of hemiaminals in water at room temperature.[10]



References

1. L.-P. Yang, X. Wang, H. Yao, W. Jiang, *Acc. Chem. Res.* **2020**, *53*, 198-208.
2. X. Huang, X. Wang, M. Quan, H. Yao, H. Ke, W. Jiang, *Angew. Chem. Int. Ed.* **2021**, *60*, 1929-1935.
3. H. Zhou, X.-Y. Pang, X. Wang, H. Yao, L.-P. Yang, W. Jiang, *Angew. Chem. Int. Ed.* **2021**, *60,* 25981-25987.
4. X. Wang, M. Quan, H. Yao, X.-Y. Pang, H. Ke, W. Jiang, *Nat. Commun*. **2022**, *13*, 2291.
5. H. Ke, L.-P. Yang, M. Xie, Z. Chen, H. Yao, W. Jiang, *Nat. Chem.* **2019**, *11*, 470.
6. L.-L. Wang, M. Quan, T.-L. Yang, Z. Chen, W. Jiang, *Angew. Chem. Int. Ed.* **2020**, *59*, 23817-23824.
7. M. Quan, X.-Y. Pang, W. Jiang, *Angew. Chem. Int. Ed.* **2022**, *61*, e202201258.
8. Y.-L. Ma, C. Sun, Z. Li, Z. Wang, J. Wei, Q. Cheng, L.-S. Zheng, X.-Y. Chang, K. Li, R. Wang, W. Jiang, *CCS Chem.* **2021**, *3*, 2143-2155.
9. L.-P. Yang, H. Ke, H. Yao, W. Jiang, *Angew. Chem. Int. Ed.* **2021**, *60*, 21404-21411.
10. M.-S. Li, Y.-W. Dong, M. Quan, W. Jiang, *unpublished results*.

I2 Stimuli Responsive Polymers via Molecular Recognition

Dalcanale E., Pinalli R., Pedrini A.

Dipartimento di Scienze Chimiche della Vita e della Sostenibilità Ambientale, Università di Parma.
E-mail: enrico.dalcanale@unipr.it

In the last few years the merging of polymer science with supramolecular chemistry has created a new, thriving field of research,[1] known under the name of supramolecular polymer chemistry.[2] The driving force behind this methodological breakthrough is the ability to control non-covalent interactions with the same precision achieved by synthetic organic chemistry. The positive fallout of this merging is demonstrated by the appearance of supramolecular polymers presenting unique mechanical, electronic, biological and self-healing properties.[1] Stimuli responsive polymers represent one of the most challenging endeavors for this research field, due to the inherent complexity to obtain specific responsiveness to external stimuli at the material level. Molecular recognition is the most sophisticated form of weak interaction in terms of precise responsiveness, since it requires a well-defined arrangement of complementary non-covalent interactions to operate at its best. Cavitands are particularly suited for the fine tuning of weak interactions due to their synthetic modularity and multiple binding modes. Using the general approach described above, we have developed several new stimuli responsive polymeric materials. Here is a selection, using cavitands as molecular receptors:

Self-diagnostic elastomers.[3] Building on our work in polymer blending with host-guest complexes,[4] we devised a supramolecular probe for the early stage stress detection in PDMS elastomers. The fluorescence probe is formed by a pyrene conjugated N-methylpyridinium salt guest in combination with a tetraphosphonate cavitand host, where the complex acts as cross-link agent. The polymer exhibits no fluorescence when the intact complex is present but a clear fluorescence emission of the guest when dissociated from the host. Under the application of stress, the weak supramolecular links within the matrix break apart, and the fluorescence of the probe is reinstated, assisting in the visualization of the stress zones and microscopic damages in PDMS.

Reusable cavitand-based electrospun membranes for polycyclic aromatic hydrocarbons (PAH) removal.[5] A highly efficient, regenerable membrane for the removal of PAHs from water, featuring excellent filter performance and pH-driven release, thanks to the integration of a cavitand receptor in electrospun polyacrylonitrile fibers will be reported. The role of the cavitand receptor is to act as molecular gripper for the uptake/release of PAHs. The regeneration of the membrane is obtained via the acid-driven opening of the cavitand to release the adsorbed PAHs, followed by the cavity restoration under basic conditions.

References

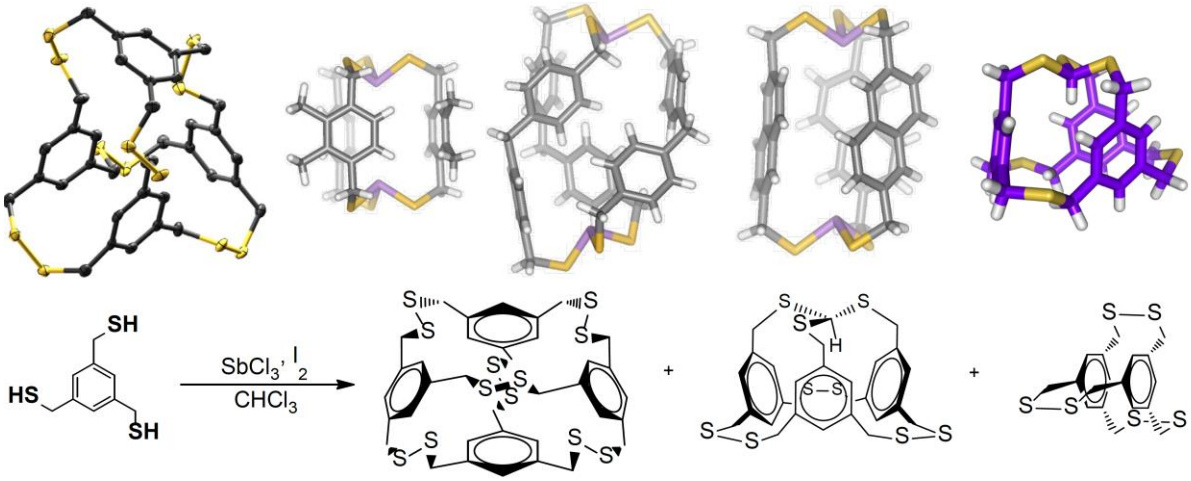
1. T. Aida, E. W. Meijer, S. I. Stupp *Science* **2012**, *335*, 813-817.
2. A. Harada, Supramolecular Polymer Chemistry, Wiley-VCH, Weinheim, **2012**.
3. A. E. Früh, F. Artoni, R. Brighenti, E. Dalcanale, *Chem. Mater.* **2017**, *29*, 7450-7457
4. M. Dionisio, L. Ricci, G. Pecchini, D. Masseroni, G. Ruggeri, L. Cristofolini, E. Rampazzo, E. Dalcanale, *Macromolecules*, **2014**, *47*, 632-638
5. M. Amorini, N. Riboni, L. Pesenti, V. A. Dini, A. Pedrini, C. Massera, C. Gualandi, F. Bianchi, R. Pinalli, E. Dalcanale *Small* **2022**, *18*, 2104946

I3 Main Group Supramolecular Chemistry: Self-Assembly of Cyclophanes, Cages, and Macrocycles

Johnson D.W., Davis W. A., Demachkie I.S., Mayhugh J. T., Shear T. A., and Zocchi L.J.

Department of Chemistry & Biochemistry and Materials Science Institute, University of Oregon, Eugene, OR, USA 97403-1253.
E-mail: dwj@uoregon.edu

Reversible metal-ligand interactions have been used as an important tool to self-assemble numerous spectacular, discrete supramolecular structures. We previously developed a design strategy for using the unusual coordination chemistry of main group ions as a directing element in self–assembly reactions to form three-dimensional, multinuclear supramolecular assemblies. For example, the trigonal pyramidal coordination geometry of Group 15-thiolates leads to self-assembly of a series of E_2L_3 "cryptands" and macrocycles (E=As, Sb) from ECl_3 and a dithiolate.[1,2]
This talk will provide a history of that chemistry in the context of new results that reveal these main group assemblies, while quite stable to air, moisture, acid and base, react cleanly with mild oxidizing agents to yield discrete disulfide macrocycles and cages (see variety pictured below). The scope of this reactivity is explored, showing that the process can efficiently prepare known and new cyclophanes, cages, and macrocycles in surprisingly efficient reactions directly from thiols under dynamic covalent control.[3,4] Efforts to explore self-sorting to prepare asymmetric assemblies and the use of "Design of Experiments" to optimize yields will also be described.[5,6]



References

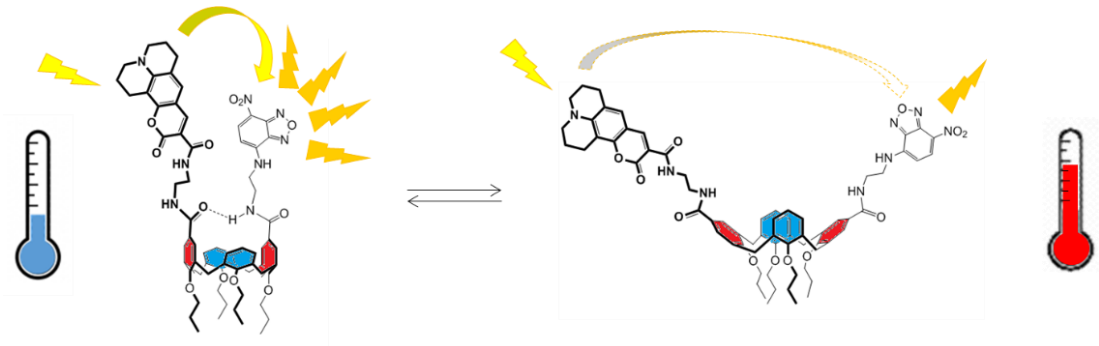
1. M. E. Carnes, M. S. Collins, D. W. Johnson, *Chem. Soc. Rev.* **2014**, 43, 1825-1834.
2. M. M. Watt, M. S. Collins, D. W. Johnson, *Acc. Chem. Res.* **2013**, *46*, 955-966.
3. M. S. Collins, N.-M. Phan, L. N. Zakharov, D. W. Johnson, *Inorg. Chem.* **2018**, *57*, 3486-3496.
4. M. S. Collins, M. E. Carnes, B. P. Nell, L. N. Zakharov, D. W. Johnson, *Nature Comm.* **2016**, *7*, 11052.
5. N.-M. Phan, T. A. Shear, L. N. Zakharov, D. W. Johnson, *Eur. J. Org. Chem.* **2020**, 6795-6800.
6. T. A. Shear, F. Lin, L. N. Zakharov, D. W. Johnson, *Angew. Chem. Int. Ed.* **2020**, *59*, 1496-1500.

C1 A Luminescent Calixarene-Based Molecular Thermometer

Baldini L., Tosi I., Faroldi F., Bardi B., Sansone F., Sissa C., Terenziani F.

Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma, Parco Area delle Scienze 17A, 43124 Parma, Italy.
E-mail: laura.baldini@unipr.it

The functionalization of calixarenes with chromophores or fluorophores has been extensively explored in the past decades and a large number of efficient molecular sensors and devices for linear and nonlinear optics applications have been reported.[1] In the last few years, we have been intrigued as well by the fascinating chemistry of dyes and, in particular, by the possibility of obtaining calixarene-dyes conjugates whose spectroscopic properties could be modulated by exploiting the peculiar conformational properties of calixarenes.
In this communication we report on the synthesis and properties of calix[4]arenes functionalized with pairs of different chromophores. Thanks to the flexibility of the calix[4]arene scaffold, we were able to control the distance between the dyes in response of an external stimulus, such as a variation of the polarity of the medium or a change of temperature. As a result, we obtained a modulation of the efficiency and dynamics of energy/electron transfer processes between the dyes[2] with potential interesting applications, such as the development of a ratiometric calixarene-based molecular thermometer.[3]



References

1. R. Kumar, A. Sharma, H. Singh, P. Suating, H. S. Kim, K. Sunwoo, I. Shim, B. C. Gibb and J. S. Kim, *Chem. Rev.* **2019**, *119*, 9657–9721.
2. I. Tosi, M. Segado Centellas, E. Campioli, A. Iagatti, A. Lapini, C. Sissa, L. Baldini, C. Cappelli, M. Di Donato, F. Sansone, F. Santoro and F. Terenziani, *ChemPhysChem*, **2016**, *17*, 1686–1706.
3. B. Bardi, I. Tosi, F. Faroldi, L. Baldini, F. Sansone, C. Sissa and F. Terenziani, *Chem. Commun.*, **2019**, *55*, 8098–8101.

C2 Cucurbit[8]uril-Secured Platinum Dimers: Recognition and Applications

Masson E.

Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701, USA.
E-mail: masson@ohio.edu

We will discuss a new recognition motif in the Cucurbituril (CB[n]) family, namely the formation of CB[8]-secured head-to-head, "stacked" platinum terpyridyl (tpy) acetylide and thiolate dimers. Both positive Pt centers sit on top of each other at one CB[8] portal, leaving the other void of any guest interaction.[1] Favorable dispersive interactions between the stacked tpy ligands and possible metal-metal bonding through d_z^2-d_z^2 orbital overlap are proposed as driving forces for the recognition pattern. We will present some self-sorting properties of these assemblies[1] and use them as catalysts for the photoreduction of water.[2] We will conclude with a rather provocative study showing that the binding selectivity of CB[n]s (n = 5 – 8), at least when guests are hydrocarbons, can be predicted by mimicking the macrocycle with a non-polar organic solvent with a "pre-formed" cavity.

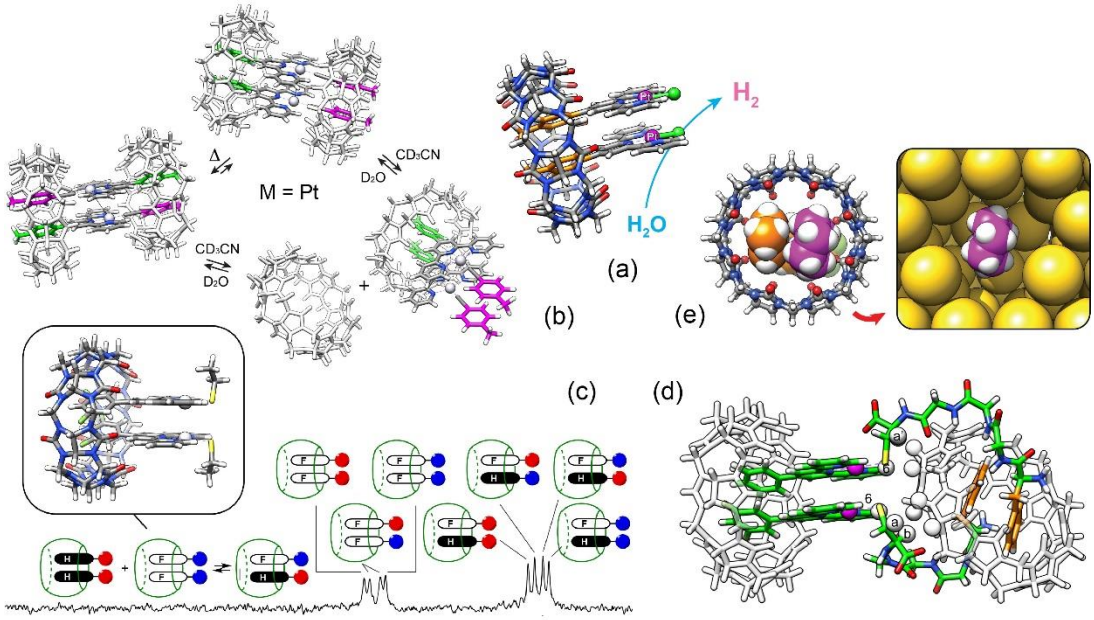


Figure 1. (a) Enhanced photoreduction of water catalyzed by a CB[8]-secured platinum dimer. (b) Orientation-specific self-assembly of Pt(II) acetylides with CB[8]. (c) "Dual layer" self-sorting between Pt thiolates and CB[8]. (d) A CB[8]-secured oligopeptide "pendant necklace". (e) Cucurbiturils mimicked by low polarizability solvents with pre-formed cavities: an empirical model to predict hydrocarbon selectivity.

References

1. a) K. Kotturi, E. Masson, *Chem. Eur. J.* **2018**, *24*, 8670 – 8678; b) H. Barbero, N. A. Thompson, E. Masson, *J. Am. Chem. Soc.* **2020**, *142*, 867 – 873. c) H. Barbero, E. Masson, *Chem. Sci.* **2021**, *12,* 9962 – 9968.
2. R. Rabbani, S. Saeedi, Md. Nazimuddin, H. Barbero, N. Kyritsakas, T. A. White, E. Masson, *Chem. Sci.* **2021**, *12*, 15347 – 15352.

C3 Pillararene Water Channels - Structural Determinants for Enhanced Filtration Performances in Bilayer and Polymeric Membranes

Barboiu M.

Institut Europeen des Membranes, Adaptive Supramolecular Nanosystems Group, University of Montpellier, ENSCM-CNRS, UMR5635, Place E. Bataillon CC047, 34095 Montpellier, France.
E-mail: mihail-dumitru.barboiu@umontpellier.fr

Artificial water channels-AWCs as their natural Aquaporin counterparts selectively transport water. They represent a tremendous source of inspiration to devise biomimetic membranes for several applications, including desalination. Herein, we critically discuss the structural details that can impact on performances of biomimetic Pillarenes as highly performant water- channels in bilayer or polyamide membranes.

The transport performances of peralkyl-carboxylate-pillar[5]arenes dimers developed by Oghosi group[1] are able to transport ~10^7 water molecules/channel/second, within one order of magnitude of AQPs' rates and opposite to their pillar[5]arene PAP counterparts selectively reject Na^+ and K^+ cations. The dimers have an tubular structure with two pillar[5]arene pores of ~5 Å supporting two narrowest twisted selectivity filters - SF of ~2.8 Å offering size restriction. This exceptional channel platform, with variable pore dimensions within the same structure is reminiscent with natural protein pores.

On the other hand, promising performances have been reported with Pillararene crystalline phases revealing impressive Å-scale separation performances, when used as selective porous materials. Self-assembled crystalline PA[5] AWCs may in-situ generated and macroscopically incorporated during the interfacial polymerization, within industrially relevant reverse osmosis polyamide-PA membranes. The optimized membranes achieve a ~40 % improvement, in water permeance of ~2.8 ± 0.5 L m^{-2} $h^{-1}bar^{-1}$ and 99.5% NaCl rejection with respect to the reference TFC membrane and a similar water permeance compared to one of the best commercial BW30 membranes (3.0 L $m^{-2}h^{-1}bar^{-1}$ and 99.5% NaCl rejection).[2]

References

1. D. Strilets, S. Fa, A. Hardiagon, M. Baaden T. Ogoshi, M. Barboiu, *Angew. Chem*. **2020**, *132(51)*, 23413-23419; *Angew. Chem. Int. Ed.* **2020**, *59(51)*, 23213-23219.
2. D. Strilets, S. Cerneaux M. Barboiu, *ChemPlusChem*, 2021, *86*,1602– 1607.

C4 Transmembrane Transport of Ions by Calixarene-based Receptors

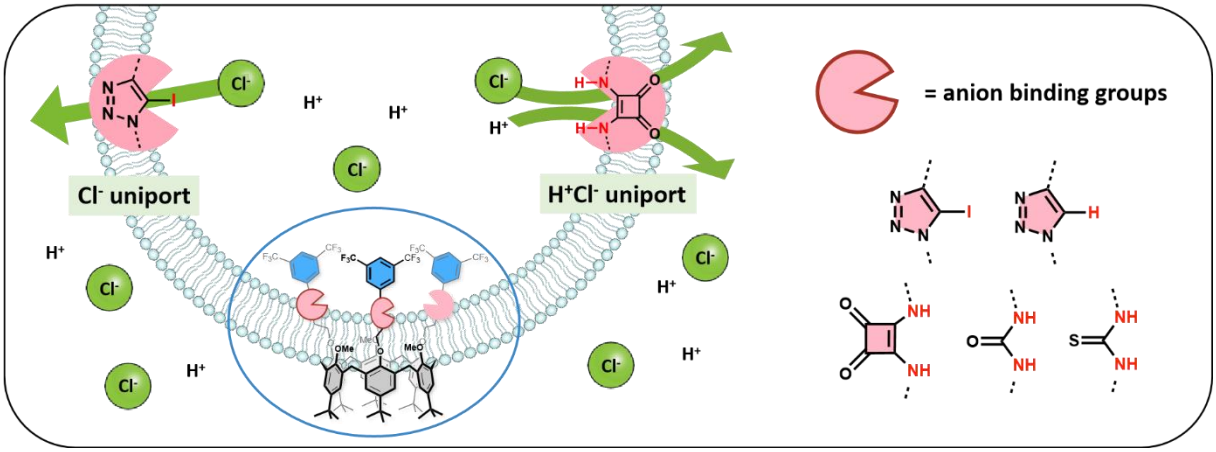
Valkenier H.

Engineering of Molecular NanoSystems, Université libre de Bruxelles, Brussels, Belgium.
E-mail: hennie.valkenier@ulb.be

Absence or malfunction of membrane proteins acting as ion channels is the cause of several channelopathies, such as cystic fibrosis. Synthetic ion carriers could take over the function of these proteins. Such carriers extract the ion from the aqueous phase into the membrane, move it across the apolar interior of the lipid bilayer while shielding its charge, to then release it on the other side of the membrane.[1]

Calixarenes have various characteristics which make them attractive scaffolds for the development of ion carriers: 1) Their lipophilicity allows them to readily partition into lipid bilayer membranes; 2) They can be easily functionalised with a wide range of groups for ion binding; 3) They have an attractive combination of preorganisation and conformational flexibility, allowing to accommodate binding groups of different sizes; 4) The cavity of calix[6]arenes can contribute to the transport of cations.[2-4]

Here, we present a series of calix[6]arene-based anion transporters and their remarkable transport properties, including >100-fold selectivity for Cl^- uniport over HCl symport when functionalised with halogen bonding donor groups.[3,4]



References

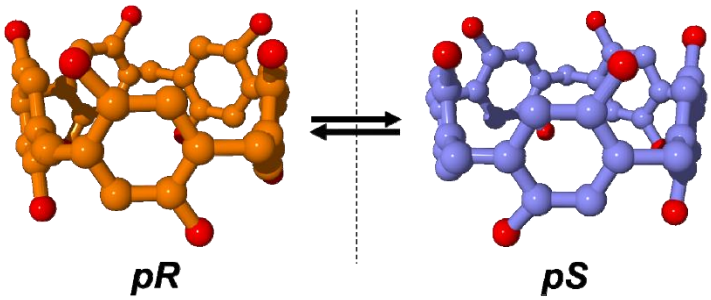
1. J. T. Davis, P. A. Gale and R. Quesada, *Chem. Soc. Rev.*, **2020**, *49*, 6056–6086.
2. N. Renier, O. Reinaud, I. Jabin and H. Valkenier, *Chem. Commun.*, **2020**, *56*, 8206–8209.
3. G. Grauwels, H. Valkenier, A. P. Davis, I. Jabin and K. Bartik, *Angew. Chem. Int. Ed.*, **2019**, *58*, 6921–6925.
4. A. Singh, A. Torres-Huerta, T. Vanderlinden, N. Renier, L. Martínez-Crespo, N. Tumanov, J. Wouters, K. Bartik, I. Jabin, H. Valkenier, *Chem. Commun.* **2022**, *under review*.

I4 Supramolecular Assemblies and Systems Constructed from Planar-Chiral Pillar[*n*]arenes

Ogoshi T.

Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto, 615-8510 Japan.
E-mail: ogoshi@sbchem.kyoto-u.ac.jp

Macrocyclic compounds play a major role in supramolecular chemistry because of their beautiful shape, nano-scale size and molecular recognition ability. Numerous supramolecular architectures have been constructed and studied as new components of materials as well as entities related to biological structural formation and functions using various macrocyclic hosts. In 2008, we reported a new class of pillar-shaped macrocyclic hosts named "pillar[*n*]arenes".[1] The specific substitution pattern of the alkoxy substituents at 1,4-positions of the benzene units makes pillar[*n*]arenes chiral, namely, planar chiral *pS* and *pR* forms. When the unit undergoes oxygen-through-the-annulus rotation, exchange between *pS* and *pR* forms (racemization) occurs.[2] In contrast, the exchange does not occur when the unit rotation is inhibited.[3] Recently, we successfully held the planar chirality for a given length of time at 25 °C in long linear guest solvents by kinetic trapping through host–guest complexation. The kinetic trapping worked at 25 °C, but not at 60 °C, thus a planar-chiral inversion using kinetic trapping based on host–guest complexation in the long linear solvents was demonstrated.[4] We also developed well-controlled planar chiral induction and memory systems and supramolecular homo-chiral dimer based on rim-differentiated pillar[5]arenes.[5–7]



References

1. a) T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi, Y. Nakamoto, *J. Am. Chem. Soc.* **2008**, *130*, 5022–5023; b) T. Ogoshi, T. Yamagishi, Y. Nakamoto, *Chem. Rev.* **2016**, *116*, 7937–8002.
2. a) T. Ogoshi, K. Kitajima, Y. Aoki, T. Yamagishi, Y. Nakamoto, *J. Phys. Chem. Lett.* **2010**, *1*, 817–821; b) S. Fa, T. Kakuta, T. Yamagishi, T. Ogoshi, *Chem. Lett.* **2019**, *48*, 1278–1287.
3. T. Ogoshi, K. Masaki, R. Shiga, K. Kitajima, T. Yamagishi, *Org. Lett.* **2011**, *13*, 1264–1266.
4. Y. Nagata, M. Suzuki, Y. Shimada, H. Sengoku, S. Nishida, T. Kakuta, T. Yamagishi, M. Suginome, T. Ogoshi, *Chem. Commun.* **2020**, *56*, 8424–8427.
5. S. Fa, K. Egami, K. Adachi, K. Kato, T. Ogoshi, *Angew. Chem. Int. Ed.* **2020**, *59*, 20353–20356.
6. S. Fa, Y. Sakata, S. Akine, T. Ogoshi, *Angew. Chem. Int. Ed.* **2020**, *59*, 9309–9313.
7. S. Fa, T. Tomita, K. Wada, K. Yasuhara, S. Ohtani, K. Kato, M. Gon, K. Tanaka, T. Kakuta, T. Yamagishi, T. Ogoshi, T. *Chem. Sci.* **2020**, in press DOI: 10.1039/D2SC00952H.

P2 The International Women in Supramolecular Chemistry Network

Hiscock J., Leigh J., Caltagirone C., Haynes C.J.E., Kieffer M., Draper E., Slater A.G., von Krbek L.K.S., Hutchins K.M., Watkins D., Busschaert N.

www.womeninsuprachem.com
E-mail: info@wisc.network, Twitter: @suprachem

The Women in Supramolecular Chemistry (WISC) network is an international network supporting the retention and progression of women and other marginalised groups within supramolecular chemistry. WISC has a unique strategy combining the "calling in" of the community with qualitative research to address equality, diversity and inclusion (EDI) issues.[1] WISC believes that change only comes through the inclusion and education of people of all genders and groups, as all these factors are intersectional. WISC wants to intervene within a space that is marginalised, and change the experiences of those entering the field, drawing on feminist and creative research practices to make sure voices are heard, and show the STEMM community that interventions like this are worthwhile and necessary.[2]

WISC's ethos is area-specific[3] and utilises a multi-modal Embodied Inquiry.[4] Creative methods are chosen to be an antidote to and represent an antithesis of those more commonly associated with 'hard' research subjects like chemistry.

In this brief introductory session, we will share insights and challenges from the creation of narrative fiction synthesised from research data[5] to highlight lived experiences. **This will give you** the opportunity to contribute to our ongoing research and public engagement projects on marginalisation, 1st Gen chemists, accessible labs, and raising the visibility of Black women in SciComm. Reflecting and sharing experiences can support the processing of lived experiences, and help form a sense of community and kinship.

WISC's approach might be unusual, but we welcome you to join us to find out more![6]

References

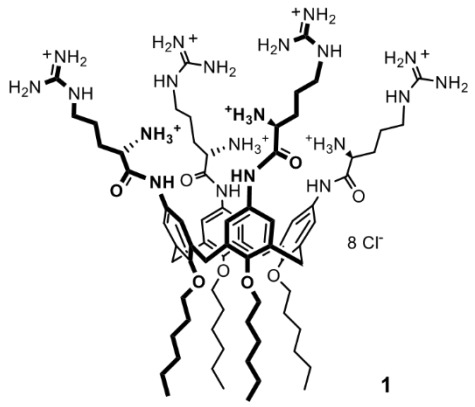
1. A. Pichon, *Nat. Chem.* **2021**, DOI 10.1038/s41557-021-00843-7.
2. J. S. Leigh, J. R. Hiscock, S. Koops, A. J. McConnell, C. J. E. Haynes, C. Caltagirone, M. Kieffer, E. R. Draper, A. G. Slater, K. M. Hutchins, D. Watkins, N. Busschaert, L. K. S. von Krbek, K. A. Jolliffe, M. J. Hardie, *CHEM* **2022**.
3. C. Caltagirone, E. Draper, C. Haynes, M. Hardie, J. Hiscock, K. Jolliffe, M. Kieffer, A. McConnell, J. Leigh, *Angew. Chemie Int. Ed.* **2021**, *60*, 11572–11579.
4. J. Leigh, N. Brown, *Embodied Inquiry: Research Methods*, Bloomsbury, London, **2021**.
5. P. Leavy, *Fiction as Research Practice: Short Stories, Novellas, and Novels*, Routledge, Abingdon, **2016**.
6. J. S. Leigh, J. R. Hiscock, C. Haynes, A. McConnell, M. Kieffer, E. Draper, K. Hutchins, D. Watkins, A. Slater, L. von Krbrek, N. Busschaert, *Women In Supramolecular Chemistry: Collectively Crafting the Rhythms of Our Work and Lives in STEM*, Policy Press, Bristol, **2022**.

I5 Calixarenes in Bionanotechnology

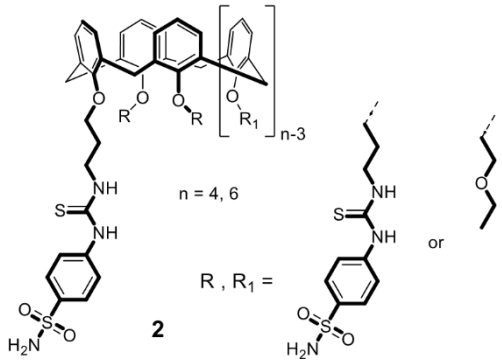
Casnati A.

Dipartimento di Chimica, Università di Parma, Parco Area delle Scienze 17/a, 43124 Parma, Italy.
E-mail: casnati@unipr.it

Calixarenes have been extensively used as scaffolds for the design of preorganized molecular receptors for ions and small molecules. In the latest 20 years, however, they became attractive as building blocks for the preparation of ligands able to interact with macromolecules of biological interest, also showing surprising and peculiar properties that strongly depend on their structure and conformation.[1] Amphiphilic cone guanidinocalixarenes (*e.g.* **1**) have been shown to self-assemble in the presence of nucleic acids of different type (DNA, RNA, PNA) and to efficiently transfect cells.[2,3] Moreover, their embedment into the outer surface of liposomes, significantly improves the cellular uptake of cargoes, thanks to the interaction with the anionic heparan-sulfate proteoglycans surrounding the cells.[4] Calixarenes have been also used, in combination with cyclodextrins, to devise novel giant amphiphiles able to self-assemble into nanospheres or nanovesicles and to deliver anticancer hydrophobic drugs to tumor cells.[5] More recently we have also prepared a small library of calix[n]arenes (*e.g.* **2**) bearing primary benzensulfonamides that demonstrated to inhibit human Carbonic Anhydrases with significant efficiency and selectivity among different isoforms of the enzymes. A mode of binding where the benzensulfonamide arm penetrates into the funnel of the enzyme active site and interacts with the protein Zn^{2+} ion is supported by X-ray diffraction data and MD calculations.[6] The knowledge acquired so far sheds a bright light on the future applications of calixarenes in bionanotechnology and nanomedicine.



1



2

References

1. L. Baldini, A. Casnati, F. Sansone, *Eur. J. Org. Chem.* **2020**, 5056–5069.
2. J. Gasparello, A. Manicardi, A. Casnati, R. Corradini, R. Gambari, A. Finotti, F. Sansone, *Scientific Reports*, **2019**, *9*, 3036. J. Gasparello, M. Lomazzi, C. Papi, E. D'Aversa, F. Sansone, A. Casnati, G. Donofrio, R. Gambari, A. Finotti, *Molecular Therapy: Nucleic Acids* **2019**, *18*, 748-763.
3. M. Lomazzi, V. Franceschi, V. Bagnacani, C. A. Vezzoni, G. Donofrio, A. Casnati, F. Sansone, *Eur. J. Org. Chem.* **2021**, 4076–4087.
4. I. Morbioli, A. Casnati, J. D. Esko, Y. Tor, F. Sansone, *Org. Biomol. Chem.*, **2021**, *19*, 6598–6602.
5. L. Gallego Yerga, C. de la Torre, F. Sansone, A. Casnati, C. Ortiz Mellet, J.-M. García Fernandez, V. Cena, *Carbohydrate Polymers*, **2021**, *252*, 117135.
6. D. Sbravati, A. Bonardi, S. Bua, A. Angeli, M. Ferraron, A. Nocentini, A. Casnati, P. Gratteri, F. Sansone, C. T. Supuran, *Chem. Eur. J.* **2022**, *28*, e202103527.

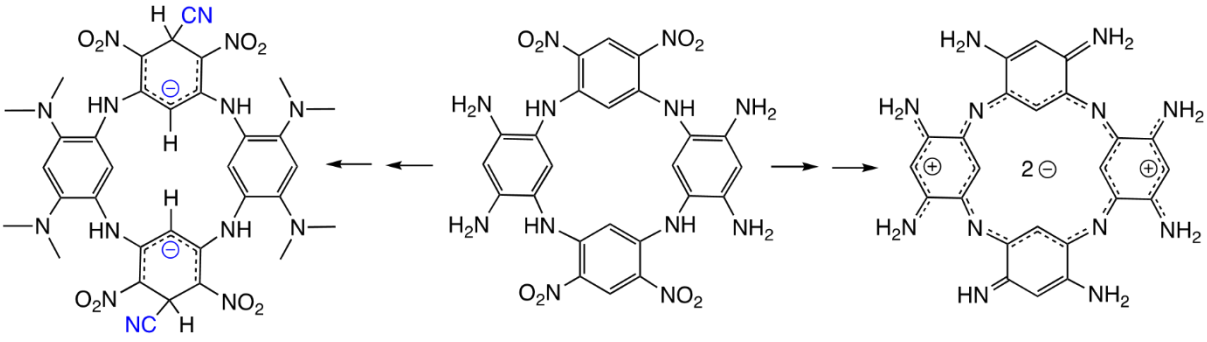
I6 Versatile Aminoazacalixarenes

Siri O.

Aix-Marseille Université, CNRS, CINaM, UMR 7325, Campus de Luminy, F-13288 Marseille cedex 09, France.

E-mail: olivier.siri@univ-amu.fr

Among the various types of heterocalixarenes, azacalixarenes are of peculiar interest since the introduction of nitrogen-bridging atoms has numerous consequences on the properties, paving the way for a wide range of applications. In this context, macrocycle of type **1** appeared recently highly versatile owing to the presence of four nitro groups and additional amino functions at the periphery and on the bridges.



3 **1** **2**

The presentation will report on our results on the aminoazacalixarene **1** as a key precursor of : 1) a new class of sophisticated receptors for anion bonding,[1] 2) a unprecedented family of porphyrin analogues **2** (azacalixphyrin)[2] absorbing in the NIR-I region, and its corresponding dimer that moves the absorption properties beyond 1000 nm (NIR-II),[3] 3) an azacalix[4]arene-based covalent organic framework as an efficient material for waste treatment,[4] and 4) a stable bis-Meisenheimer complex that can be viewed as an emerging class of anionic macrocycles.[5]

The access to these derivatives and the mentioned properties will be described and discussed.

References

1. a) G. Canard, J. Andeme Edzang, Z. Chen, M. Chessé, M. Elhabiri, M. Giorgi, O. Siri *Chem. Eur. J.* **2016**, *22*, 5756. b) Z. Chen, G. Canard, C. Azarias, D. Jacquemin, O. Siri *New J. Chem*. **2017**, *41*, 5284.
2. Z. Chen, M. Giorgi, D. Jacquemin, M. Elhabiri, O. Siri *Angew. Chem. Int. Ed*., **2013**, *52*, 6250. b) L. Lavaud, S. Pascal, K. Metwally, A. Da Silva, Z. Chen, M. Elhabiri, G. Canard, D. Jacquemin, O. Siri *Chem. Commun*. **2018**, *54*, 12365. c) L. Lavaud, C. Azarias, G. Canard, S. Pascal, D. Jacquemin, O. Siri *New J. Chem*. **2020**, *44*, 18130. d) L. Breloy, R. Mhanna, J.-P. Malval, V. Brezová, D. Jacquemin, S. Pascal, O. Siri, D.-L. Versace *Chem. Commun*., **2021**, 57, 8973.
3. L. Lavaud, C. Azarias, G. Canard, S. Pascal, J. Galiana, M. Giorgi, Z. Chen, D. Jacquemin, O. Siri *Chem. Commun.* **2020**, *56,* 896.
4. T. Skorjanc, D. Shetty, F. Gándara, S. Pascal, N. Naleem, L. Ali, A. K. Mohammed, J. Raya, S. Kirmizialtin, O. Siri, A. Trabolsi. **2022**, *submitted.*
5. A. Torres Ruiz, S. Pascal, D. Jacquemin, G. Canard, J.-M. Raimundo, P. Vanloot, O.Siri, **2022**, *submitted.*

I7 Prismarenes: A Novel, Promising Class of Macrocyclic Host Molecules

Gaeta C.

Laboratory of Supramolecular Chemistry, Department of Chemistry and Biology "A. Zambelli", University of Salerno, Via Giovanni Paolo II, Fisciano, I-84084, Italy.
E-mail: cgaeta@unisa.it

Since 1967, when Charles Pedersen reported the first template-synthesis of crown-ethers, a plethora of peculiar macrocyclic structures have been designed and obtained by guest-templated strategies. Recently we have reported a novel class of macrocyclic hosts, based on methylene-bridged 1,5-naphthalene units, named prismarenes.[1-5] This novel class of macrocycles, has been obtained by a templated approach of a thermodynamically controlled synthesis.[1] Prismarene macrocycles have an π-electron-rich aromatic cavity and prism-like structures that inspired the prismarene name (Figure "b").[6] Prism[n]arene hosts show a good affinity for ammonium guests and form complexes stabilized by cation···π and $^{+}$NC−H···π interactions, both in organic and aqueous medium. In this communication, we will discuss aspects related to the synthesis, structural properties, and recognition abilities of this new class of macrocyclic hosts.

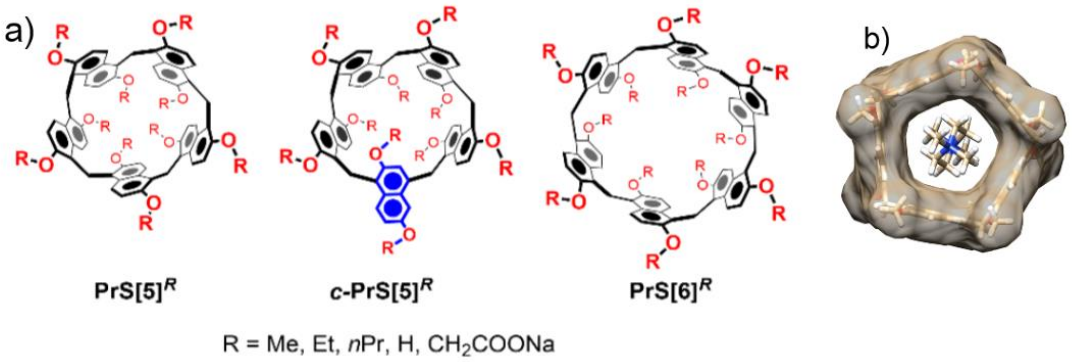


Figure 1. a) Chemical drawing of prismarene macrocycles. b) X-ray structural model of the host-guest complex between *N,N,N',N'*-tetramethylpiperazonium cation and prism[5]arene **PrS[5]^{Me}**.

References

1. P. Della Sala, R. Del Regno, C. Talotta, A. Capobianco, N. Hickey, S. Geremia, M. De Rosa, A. Spinella, A. Soriente, A. Spinella, P. Neri, C. Gaeta, *J. Am. Chem. Soc*. **2020**, *142*, 1752–1756.
2. Reference 1 was highlighted in: L.-P. Yang, W. Jiang, *Angew. Chem. Int. Ed.* **2020**, *7*, 15794–15796.
3. P. Della Sala, R. Del Regno, L. Di Marino, C. Calabrese, C. Palo, C. Talotta, S. Geremia, N. Hickey, A. Capobianco, P. Neri, C. Gaeta, *Chem. Sci*. **2021**, *12*, 9952–9961.
4. R. Del Regno, P. Della Sala, D. Picariello, C. Talotta, P. Neri, C. Gaeta, *Org. Lett*. **2021**, *23*, 8143–8146.
5. R. Del Regno, G. D. G. Santonoceta, P. Della Sala, M. De Rosa, A. Soriente, C. Talotta, A. Spinella, P. Neri, C. Sgarlata, C. Gaeta, *Org. Lett*. **2022**, https://doi.org/10.1021/acs.orglett.2c00819.
6. Thanks are due to prof. Wei Jiang for suggesting "prismarene" as the name to be given to these molecules.

F1 Ionic Resorcinarenes Target Pyrophosphate and αA66-80 Peptide Related to Cataracts

Beyeh N. K.

Department of Chemistry, Oakland University, 146 Library Drive, Rochester, MI 48309-4479, USA
E-mail: beyeh@oakland.edu

Cavity-containing macrocyclic compounds can be modified with specific functional groups and used as a target for biological materials.[1] Though it is a significant challenge to develop high-affinity receptors for anions in biologically relevant solvents, designing synthetic macrocycles that can target small bioanalytes, peptides or proteins offer a suitable avenue for applications in hybrid materials, diagnostics, and aggregation inhibitors.[2] In this talk, I will present results from two such projects:
1) Pyrophosphate (PPi) and adenosine triphosphate (ATP) are key intermediates for energy transduction and are common to several essential metabolic processes. Several diseases are strongly associated with elevated PPi levels, including cancer, arthritis, crystal deposition disease, and Paget's disease. Significant recent research effort has been focused on developing more potent PPi sensors for the early diagnosis of these conditions. We use cationic resorcinarenes and in some cases, integrated with a fluorescent tag as simple read-out high-affinity sensors for pyrophosphate.[3]
2) The αA66-80 peptide fragment of αA-crystallin, among others, was observed at a high level in cataracts eye lenses. The αA-crystallin, a heat-shock protein, maintains the solubility and stability of lens proteins and lens clarity by preventing protein aggregation, which may lead to lens clouding and eventually cataracts. We use three different ionic resorcinarene macrocycles to study how they affect αA66-80 peptide aggregation and inhibition (Figure 1).[4]

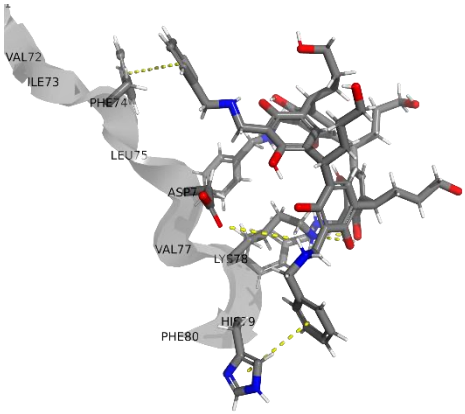


Figure 1. A resorcinarene αA66-80 peptide complex

References

1. T. Douglas, M. Young, *Nature* **1998**, *393*, 152–155.
2. A. E. Hargrove, S. Nieto, T. Zhang, J. L. Sessler, E. V. Anslyn, *Chem. Rev.* **2011**, *111*, 6603–6782.
3. N. K. Beyeh, I. Díez, S. M. Taimoory, D. Meister, A. Feig, J. F. Trant, R. H. A. Ras, K. Rissanen, *Chem. Sci.* **2018**, *9*, 1358-1367; b) K. Twum, S. I. Sadraei, J. Feder, S. M. Taimoory, K. Rissanen, J. F. Trant, N. K. Beyeh, *Org. Chem. Front.* **2022,** *9*, 1267-1275.
4. K. Twum, A. Bhattacharjee, E. T. Laryea, J. Esposto, G. Omolloh, S. Mortensen,M. Jaradi, N. L. Stock, N. Schileru, B. Elias, E. Pszenica, T. M. McCormick, S. Martic, N. K. Beyeh, *RSC Med. Chem.* **2021**, *12*, 2022-2030.

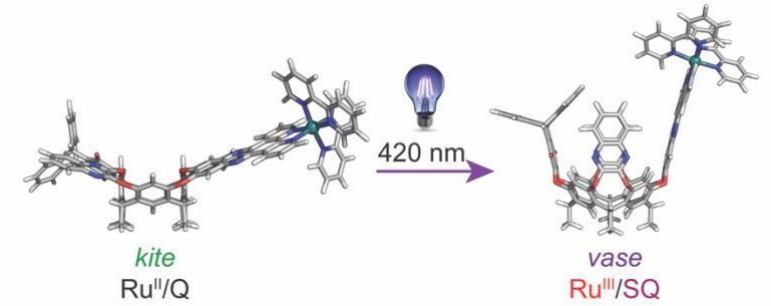
F2 Stimuli-Responsive Resorcin[4]arene Cavitands: Toward Visible Light-Activated Molecular Grippers

García-López V,[a,b] Zalibera M.,[c] Trapp N.,[b] Wenger O. S.,[d] Diederich F.[b]

[a] Department of Chemistry, Louisiana State University, 349 Chemistry and Materials Building, Baton Rouge LA 70806; [b] Laboratory of Organic Chemistry, ETH Zurich, HCI Vladimir-Prelog-Weg 3, Zurich, Switzerland 8093; [c] Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology, Radlinského 9, Bratislava, Slovakia 81237; [d] Department of Chemistry, University of Basel, St. Johanns-Ring 19, Basel Switzerland 4056.

E-mail: vglopez@lsu.edu

We synthesized and investigated a series of multi-stimuli responsive resorcin[4]arene cavitands equipped with quinone (**Q**) and $[Ru(bpy)_2dppz]^{2+}$ photosensitizing walls in different configurations. The cavitands exhibit a large conformational switching from an expanded *kite* to a contracted *vase* with a deep cavity upon visible light irradiation, chemical and electrochemical redox activation, and hostguest interactions in the ground state. Upon visible light irradiation, electron transfer from the $[Ru(bpy)_2dppz]^{2+}$ to the **Q** generates the semiquinone (**SQ**) radical anion, triggering the large conformational switching. Depending on the molecular design, the **SQ** radical can live for several minutes (~10 min), and the *vase* can be generated in a secondary process without the addition of a sacrificial electron donor. These systems overcome three limitations of previous designs: the need for a sacrificial donor to accumulate the short-living **SQ** (~ s), and the inability to form a *vase*, and capture guest molecules. This study provides insights into the development of stimuli-responsive molecular grippers for transmembrane delivery, nanofabrication, sensor technologies, or switchable units in materials that require significant conformational changes.



References

1. a) V. García-López, M. Zalibera, N. Trapp, M. Kuss-Petermann, O. Wenger, F. Diederich, *Chem. Eur. J.* **2020**, *26*, 11451–11461; b) V. García-López, J. Milić, M. Zalibera, D. Neshchadin, M. Kuss-Petermann, L. Ruhlmann, J. Nomrowski, N. Trapp, C. Boudon, G. Gescheidt, O. S. Wenger, F. Diederich, *Tetrahedron* **2018**, *74*, 5615–5626.

F3 Novel Silica-Bound Supramolecular Chromatographic Stationary Phases

Mekapothula S.R.,[a] Wonanke A.D.D.,[a] Addicoat M.A.,[a] Boocock D.J.,[b] Cragg P.J.,[c] Wallis J.D.,[a] and Cave G.W.V.[a]

[a] Nottingham Trent University, School of Science and Technology, Clifton Lane, Nottingham, UK; [b] The John van Geest Cancer Research Centre, School of Science and Technology, Clifton Lane, Nottingham, UK; [c] School of Pharmacy and Biomolecular Science, Huxley Building, University of Brighton, Brighton, UK.

E-mail: subba.mekapothula@ntu.ac.uk

A novel co-pillar[4+1]arene incorporating bromo-octyl substituents has been synthesized for the first-time using microwave irradiation with high yield (88%) and subsequently bound to the surface of chromatographic silica particles. The resulting new stationary phase has been successfully utilized to separate all xylene isomers *via* the flash column chromatography technique.[1] To demonstrate the versatility of this new class of stationary phases, a silica immobilized co-pillar[4+1]arene supramolecular cavitand has been designed in-silico using host-guest binding energy studies, and realized experimentally to selectively interact with a range of peptides *via* their morphology and amino acid functionalities. The new computationally designed column demonstrates superior separation of five peptides (15-20 residues) compared to a traditional RP-C_{18} LC-MS/MS stationary phase.[2]

A silica-bound *C*-butylpyrogallol[4]arene chromatographic stationary phase was also prepared to evaluate both the preparative and analytical scale chromatographic separation of C_{60} and C_{70} fullerenes in reverse phase mode *via* flash column chromatography and HPLC. The two fullerenes were separated on this phase by size-selective molecular recognition as postulated from our in-silico studies.[3]

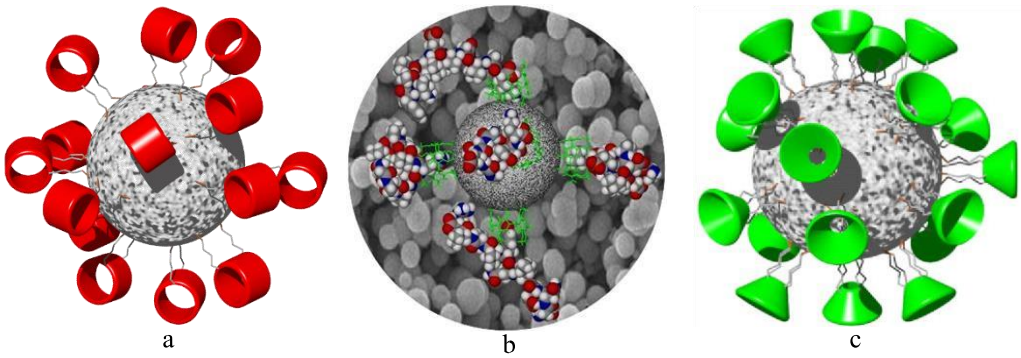


Figure 1. Co-pillar[4+1]arene bound silica flash column (a), UPLC (b), and *C*-butylpyrogallol[4]arene stationary phase

References

1. S. Mekapothula, M. A. Addicoat, D. J. Boocock, P. Cragg, J. D. Wallis and G. W. V. Cave, *Chem. Commun*. 2020, **56**, 1792-1794.
2. S. Mekapothula, A. D. D. Wonanke, M. A. Addicoat, D. J. Boocock, J. D. Wallis and G. W. V. Cave, *New J. Chem.*, 2021, **45**, 141-146.
3. S. Mekapothula, A. D. D. Wonanke, M. A. Addicoat, D. J. Boocock, J. D. Wallis, and G. W. V. Cave, *Int. J. Mol. Sci.*, 2021, **22**, 5726.

F4 Large-Scale, Chromatography-Free Ethoxypillar[6]arene Synthesis

Wilson C. R., Chen E. F. W., Puckett A. O., Hof F.

University of Victoria, Department of Chemistry, Victoria, British Columbia, Canada.
E-mail: crwilson@uvic.ca

Pillar[n]arenes are a family of macrocycles that have quickly become important in supramolecular chemistry. Pillar[5]arene[1] is the most commonly studied pillar[n]arene, however its small internal cavity limits its applications. The larger pillar[6]arene[2] is a highly desired host. The sulfated analog (PillarMaxQ) has been shown to bind biologically relevant guests with picomolar affinity.[3] Ethoxypillar[6]arene (EtOP6) is a key intermediate in the formation of many pillar[6]arene derivatives. Quick and easy access to this initial scaffold is key for new functionalization methods and further applications. Access to this analog however is currently limited, as the formation of pillar[6]arene is disfavored in the cyclization reaction, predominantly resulting in the less strained pillar[5]arene. Alkoxy-protected pillar[6]arenes are generally made through a solvent-templated Friedel–Crafts cyclization. While there are many reported methods to make ethoxypillar[6]arene, they have significant downfalls. They are not ring-size selective, they require unusual protecting groups, and/or they are run on small scales. Published methods require difficult separations of pillar[5]arene and other pillar[n]arene byproducts. To overcome these shortcomings, we developed a method that exclusively makes ethoxypillar[6]arene, thus avoiding the need for chromatographic purification. Our method can be run on scales from 1 to 40 grams. Easier access to ethoxypillar[6]arene will help enable new host-guest chemistry, functionalization methods and novel derivatives of pillar[6]arene.

References

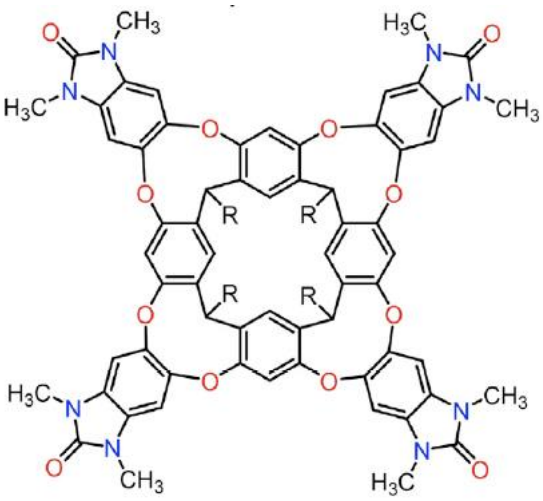
1. T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi, Y. Nakamoto, *J. Am. Chem. Soc.* **2008**, *130*, 5022-5023.
2. D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang, H. Meier, *Angew. Chem. Int. Ed.* **2009**, *48*, 9721-9723.
3. W. Xue, P. Y. Zavalij, L. Isaacs, *Angew. Chem. Int. Ed.* **2020**, *59*, 13313-13319.

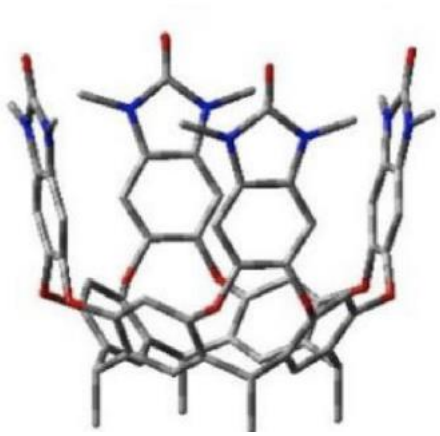
P3 Molecules Under Confinement

Rebek J., Yu Y.

Center for Supramolecular Chemistry and Catalysis and Department of Chemistry, Shanghai University, 99 Shang-Da Road, Shanghai 200444, China.
E-mail: jrebek@scripps.edu

This lecture follows the course of reactions that take place in container compounds. The containers are deep, open-ended compounds – cavitands – that largely surround their target molecules and confine their motions. The selectivity of the recognition event and the forces involved are described. Progress on the development of water-soluble cavitands and their applications to difficult macrocyclizations and separations are reported. The chemical structure and vase-like shape of a deepened cavitand is shown below.





References

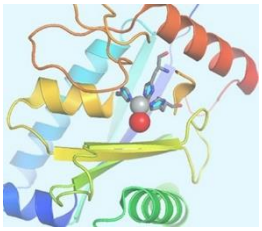
1. Y. Zhu, M. Tang, H. Zhang, F.-U. Rahman, P. Ballester, J. Rebek Jr., C. A. Hunter, Y. Yu, *J. Am. Chem. Soc.* **2021***, 143,* 12397-12403.
2. J.-M. Yang, Y.-Q. Chen, Y. Yu, P. Ballester, J. Rebek Jr, *J. Am. Chem. Soc.* **2021**, *143,* 19517-19524.

P4 A Biomimetic Cavity, a Metal Ion and Water: A Trialogue Full of Surprises!

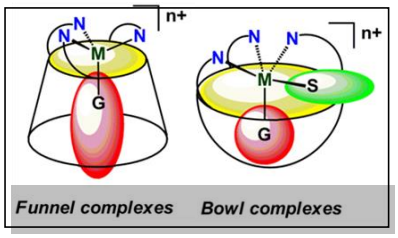
Reinaud O.

Université de Paris Cité, Laboratoire de Chimie et Biochimie, CNRS UMR 8601, 45 rue des Saints Pères, 75006 Paris, France.
E-mail: Olivia.Reinaud@parisdescartes.fr

Molecular recognition in a confined space is a classical event in biology, at the basis of essential processes such as signaling or catalysis. A metal ion is often associated with it, active as a Lewis acid or redox center. The third element inevitably present is water, either as a solvent or as a molecular actor involved in recognition or catalysis phenomena. Having developed biomimetic cavity systems capable of binding and thus controlling the reactivity of a metal ion,[1-3] we are interested in the particular role that water can play as a solvent but also as a molecule interacting with the cavity complexes. A set of surprising results obtained with calixarenes[1,4] and resorcinarenes[5-8] ("funnel" and "bowl" complexes) will be presented.



Proteic metallo-site



Supramolecular modelling

References

1. N. Le Poul, Y. Le Mest, I. Jabin, O Reinaud, *Acc. Chem. Res.*, **2015**, *48*, 2097–2106. DOI: 10.1021/acs.accounts.5b00152
2. J.-N. Rebilly, B. Colasson, O. Bistri, D. Over, O. Reinaud, *Chem. Soc. Rev.* **2015**, *44*, 467-489. DOI: 10.1039/c4cs00211c
3. O. Bistri and O. Reinaud, *Org. Biomol. Chem.,* **2015**, *13*, 2849–2865. DOI: 10.1039/C4OB02511C
4. N. Le Poul, B. Colasson, G. Thiabaud, D. Jeanne Dit Fouque, C. Iacobucci, A. Memboeuf, B. Douziech, J. Řezáč, T. Prangé, A. de la Lande, O. Reinaud, Y. Le Mest, *Chem. Sci.* **2018**, *9*, 8282–8290. DOI: 10.1039/C8SC03124J 5. E. Brunetti, L. Marcelis, F. E. Zhurkin, M. Luhmer, I. Jabin, O. Reinaud, K. Bartik, *Chem. Eur. J.* **2021**, *27*, 13730–13738. DOI: 10.1002/chem.202102184.
6. S. Collin, A. Parrot, L. Marcelis, E. Brunetti, I. Jabin, G. Bruylants, K. Bartik, and O. Reinaud, *Chem. Eur. J.* **2018**, *24*, 17964 –17974. DOI: 10.1002/chem.201804768.
7. A. Parrot, S. Collin, G. Bruylants, O. Reinaud, *Chem. Sci.* **2018,** *9*, 5479–5487. DOI: 10.1039/c8sc01129j.
8. S. Collin, N. Giraud, E. Dumont, O. Reinaud, *Org. Chem. Front.*, **2019**, *6*, 1627–1636. DOI: 10.1039/c9qo00263d

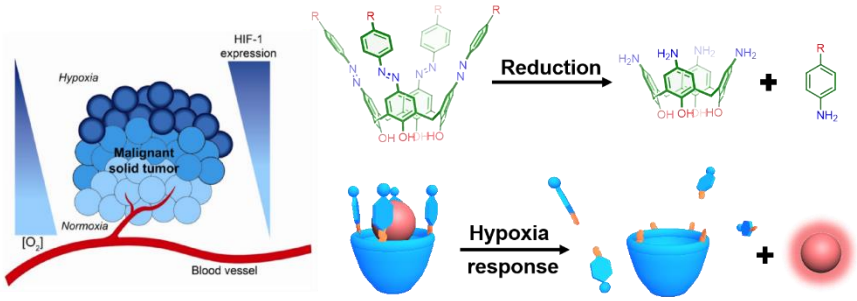
I8 Hypoxia-Responsive Drug Delivery System Based on Azocalixarenes

Guo D.-S.

College of Chemistry, Nankai University, Tianjin 300071, China.
E-mail: dshguo@nankai.edu.cn

Host-guest recognition provides new supramolecular formulations that improve the solubility, stability, and bioavailability of drugs, reduce side effects, and achieve targeted drug delivery. Moreover, macrocycles are one class of carriers possessing precise molecular structure/weight, and offering an exact cavity-loading pattern for drug and a quantifiable binding constant. As a result, macrocyclic delivery systems present the advantages of easy construction, molecular-level protection, quantitative loading, controlled release, reproducibility and multidrug adaptability. Supramolecular formulations represent a novel type of drug formulation with predictable therapeutic indices and have excellent application prospects from the viewpoints of both scientific research and industry. To meet the needs of precise delivery, designed macrocycles are expected to afford strong binding of drugs with excellent selectivity towards biologically co-existing species to avoid premature dissociation, and have stimuli-responsiveness to accomplish controlled release.

As part of our ongoing research on supramolecular biomedical materials, we designed a series of azocalixarenes, and explored their drug delivery capabilities. These azocalixarenes, with vertically expanded deep cavity, show high binding affinities to many biomedical molecules, including bioimaging agents, chemotherapeutic drugs, radiotherapeutic drugs as well as photothermal agents. Moreover, azocalixarene carriers are hypoxia-responsive that achieve targeted delivery. Hypoxia is a typical characteristic of many diseases, including tumor, kidney injury, bacterial infection, rheumatoid arthritis and stroke. We therefore realized the selective imaging, targeted therapy, theranostics, and combinational therapy for these diseases *in vivo*.



References

1. W.-C. Geng, S. Jia, Z. Zheng, Z. Li, D. Ding, D.-S. Guo, *Angew. Chem. Int. Ed.* **2019**, *58*, 2377–2381.
2. T.-X. Zhang, Z.-Z. Zhang, Y.-X. Yue, X.-Y. Hu, F. Huang, L. Shi, Y. Liu, D.-S. Guo, *Adv. Mater.* **2020**, *32*, 1908435.
3. Z. Zhang, Y.-X. Yue, L. Xu, Y. Wang, W.-C. Geng, J.-J. Li, X.-l. Kong, X. Zhao, Y. Zheng, Y. Zhao, L. Shi, D.-S. Guo, Y. Liu, *Adv. Mater.* **2021**, *33*, 2007719.
4. Y.-Q. Cheng, Y.-X. Yue, H.-M. Cao, W.-C. Geng, L.-X. Wang, X.-Y. Hu, H.-B. Li, Q. Bian, X.-L. Kong, J.-F. Liu, D.-L. Kong, D.-S. Guo, Y.-B. Wang, *J. Nanobiotechnol.* **2021**, *19*, 451.
5. X. Hou, Y.-X. Chang, Y.-X. Yue, Z.-H. Wang, F. Ding, Z.-H. Li, H.-B. Li, Y. Xu, X. Kong, F. Huang, D.-S. Guo, J. Liu, *Adv. Sci.* **2022**, *9*, 2104349.

I9 From Calixarenes to Zigzag Hydrocarbon Nanobelts

Wang M.-X.

Department of Chemistry, Tsinghua University, Beijing, China.
E-mail: wangmx@mail.tsinghua.edu.cn

Zigzag hydrocarbon belts such as belt[n]arenes or [n]cyclacenes and their partially hydrogenated analogs (Figure 1) have been fascinating chemists and materials scientists for decades because of their aesthetically appealing molecular structures, tantalizing physical properties and intriguing chemical reactivities. They are unique and useful macrocyclic hosts in supramolecular chemistry. They may also serve as templates or seeds to grow structurally well-defined uniform zigzag carbon nanotubes. Despite synthetic effort in the past decades, the synthesis of zigzag hydrocarbon belts remains a great challenge. Very recently, we[1-3] have reported a general and straightforward fjord-stitching strategy to construct zigzag hydrocarbon belts from inexpensive and easily available resorcin[n]arenes. The method has been extended to the synthesis of edge-functionalized zigzag hydrocarbon belts and heteroatom-embedded zigzag hydrocarbon belts. Aromatization of octahydrobelt[8]arene with an access amount of DDQ led to the formation of a belt[8]arene-(DDQ)4 adduct which underwent probably retro-Diels-Alder reaction, allowing the observation of the first fully conjugated zigzag hydrocarbon belt. In this talk, I will focus on the synthesis and structures of zigzag hydrocarbon belts from calixarenes. Perspectives on the strategies to isolate and characterize the fully conjugated belt[n]arenes and on the applications of zigzag hydrocarbon belts are also discussed.

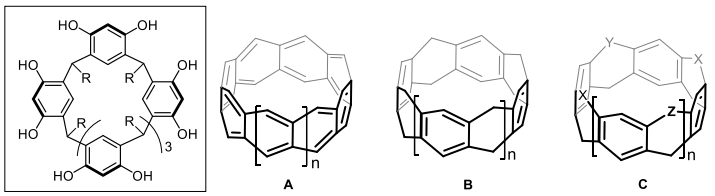


Figure 1. Resorcin[n]arenes and zigzag hydrocarbon nanobelts.

References

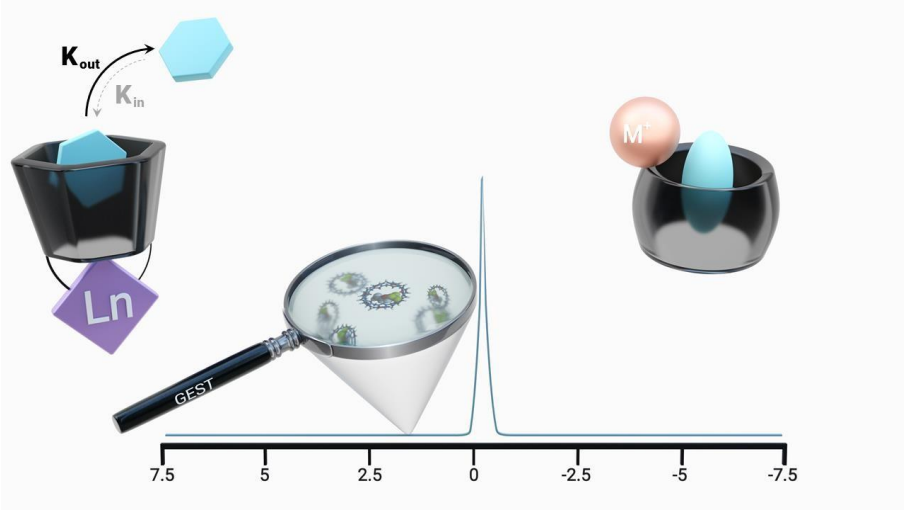
1. (a) Q. Zhang, Y.-E. Zhang, S. Tong, M.-X. Wang, *J. Am. Chem. Soc.* **2020**, *142*, 1196-1199. (b) T.-H. Shi, Q.-H. Guo, S. Tong, M.-X. Wang, *J. Am. Chem. Soc.* **2020**, *142*, 4576-4580. (c) T.-H. Shi, S. Tong, M.-X. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 7700-7705. (d) Y. Zhang, S. Tong, M.-X. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 18151-18155. (e) M.-L. Tan, Q.-H. Guo, X.-Y. Wang, T.-H. Shi, Q. Zhang, S.-K. Hou, S. Tong, J. You, M.-X. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 23649-23658. (f) M. Xie, S. Tong, M.-X. Wang, *CCS Chem.* **2022**, in press.
2. For an overview on zigzag hydrocarbon belts, see: T.-H. Shi, M.-X. Wang, *CCS Chem.* **2020**, *2*, 916-931.
3. For a review on zigzag and other type aromatic molecular belts, see: Q.-H. Guo, Q., Qiu, M.-X. Wang, J. F. Stoddart, *Nat. Chem.* **2021**, *13*, 402-419.

I10 Elucidating Dynamics in Host-Guest Systems: a GEST NMR Approach

Avram L. and Bar-Shir A.

Faculty of Chemistry, Weizmann Institute of Science, 7610001 Rehovot, Israel.
E-mail: liat.avram@weizmann.ac.il

Binding kinetics is a key feature in supramolecular systems, which significantly influences their self-assembly in solution. Specifically in host-guest systems, dynamic processes such as guest exchange are responsible for their unique properties and applications. However, both the dynamic exchange and the relatively low concentration of an obtained host-guest complex reduce the sensitivity and limit the efficiency of the currently available analytical tools to explore such processes. GEST[1] (Guest Exchange Saturation Transfer) is an NMR technique that allows the detection of micromolar—and even nanomolar—concentrations of a complex with only a few scans. In addition, by fitting the GEST data to computational simulations, the exchange rate of free and bound guest and the fractional occupancy of the host can be evaluated. ^{19}F-GEST experiment was used to extract exchange rates and activation energy for fast exchanging guests in the presence of cucurbit[n]urils.[2] The effect of monovalent cations on the extracted activation energy was also tested.[2] This method was also used as a platform for multi-color applications as was demonstrated by systems such as octa-acid[3] and lanthanide-cradled cyclodextrin.[4] Since the GEST experiment can be easily implemented in any conventional NMR setup, this approach could expand the analytical toolbox available to study dynamic host-guest systems in solution.



References

1. L. Avram and A. Bar-Shir, *Org. Chem. Frontiers*, **2019**, *6*, 1503-1512.
2. R. Shusterman-Krush, L. Grimm, L. Avram, F. Biedermann and A. Bar-Shir, *Chem. Sci.*, **2021**, *12*, 865-871.
3. R. Shusterman-Krush, N. D. Tirukoti, A. K. Bandela, L. Avram, H. Allouche-Arnon, X. Cai, B. C. Gibb and A. Bar-Shir, *Angew.Chem. Int. Ed.* **2021**, *60*, 15405–15411.
4. E. Goren, L. Avram and A. Bar-Shir, *Nat. Commun.*, **2021**, *12*, 3072-3079.

C5 Modulating Electrochemical Activity Through Encapsulation

Elgrishi N., Bujol R. J., Das Bairagya M., and Grundhoefer J. P.

Louisiana State University, 232 Choppin Hall, Baton Rouge, Louisiana 70803, United States.
E-mail: noemie@lsu.edu

Transition metal based molecular catalysts for solar fuel production are advantageous as they are amenable to fundamental mechanistic studies. These studies help refine catalyst design to control and optimize the conversion of energy-poor feedstocks into fuels, either photo-catalytically or electrochemically.[1] A wide library of molecular electrocatalysts is available, but many are plagued by the prevalence of degradation caused by product inhibition and multimetallic deactivation pathways.[2] Concurrently, molecular containers have been demonstrated to encapsulate various organic and inorganic species, with a recent emphasis on encapsulating molecular catalysts.[3] As interest in molecular electrocatalysts continues to increase, in particular for energy storage applications, our long-term focus is on investigating the figures of merit of molecular metallocages to modulate the secondary coordination sphere of fuel producing molecular electrocatalysts.[4] We report on our work investigating the effect of encapsulation on electrochemical properties using redox active guests as electrochemical probes. Understanding the effect of site isolation, controlled encapsulation, and pore size on impacting the efficiency and selectivity of molecular electrocatalysts will contribute to bridging the gap between homogeneous and heterogeneous molecular catalysis.

References

1. S. Dasgupta, B. S. Brunschwig, J. R. Winkler, H. B. Gray, *Chem. Soc. Rev.* **2013**, *42*, 2213–2214.
2. K. J. Lee, B. D. McCarthy, J. L. Dempsey, *Chem. Soc. Rev*. **2019**, *48*, 2927–2945.
3. a) H. Amouri, C. Desmarets, J. Moussa, *Chem. Rev.* **2012**, *112*, 2015–2041. b) L. J. Jongkind, X. Caumes, A. P. T. Hartendorp, J. N. H. Reek, *Acc. Chem. Res.* **2018**, *51*, 2115–2128. c) D. Zhang, T. K. Ronson, J. R. Nitschke, *Acc. Chem. Res.* **2018**, *51*, 2423–2436. d) N. Hosono, S. Kitagawa, *Acc. Chem. Res.* **2018**, *51*, 2437–2446. e) C. M. Hong, R. G. Bergman, K. N. Raymond, F. D. Toste, *Acc. Chem. Res.* **2018**, *51*, 2447–2455.
4. M. Das Bairagya, R. J. Bujol, N. Elgrishi, *Chem. Eur. J.* **2020**, *26*, 3991–4000.

C6 A Protonated Hemicryptophane for Selective Binding of Polar Guests and Anions

Lin Y., Du K., Gau M. R., Carroll P. J., Dmochowski I. J.

Department of Chemistry, University of Pennsylvania, 231 S. 34th St., Philadelphia, Pennsylvania 19104.

E-mail: linyann@sas.upenn.edu

The affinity of small molecules for biomolecular cavities is tuned through a combination of primary and secondary interactions. It has been challenging to mimic these features in organic synthetic host molecules, however, where the cavities tend to be highly symmetric and nonpolar, and less amenable to chemical manipulation. Inspired by the host-guest properties of calix[6]arenes reported by Reinaud and Jabin,[1,2] we sought to enhance the binding affinity of a hemicryptophane host ***L*** (Figure 1), formed by the linkage of a cyclotriveratrylene cap with a tris(2-aminoethyl)amine (TREN) ligand. Protonating the TREN moiety with various sulfonic acids polarized the cavity. Interestingly, the sulfonate counteranions form hydrogen bonds at the apertures of the cavity (Figure 2), thereby regulating small-molecule access and binding affinity in organic solution. TREN protonation provides a versatile method for installing counteranions with widely varying stereoelectronic properties. This work highlights the opportunity to generate a diverse set of peripherally tuned, biomimetic cavities from H_3TREN-hemcryptophane and reveals "counteranion tuning" to be a simple and powerful strategy for modulating host-guest affinity.[3]

Triply protonated hemicryptophane ***H_3L*** is also amenable for studying anion binding in aqueous solution. Highly selective fluoride encapsulation was evidenced by ^{1}H NMR, ^{19}F NMR and X-ray crystallography (Figure 3). In addition, the protonated capsule exhibited an exclusive 'turn-on' fluorescence signal upon fluoride addition. An 'apparent' association constant [$K_{app} = (4.0 \pm 0.3) \times 10^5$ M^{-1}] and a detection limit of 120 nM were extracted from the fluorescence titration experiments in H_2O. Finally, the protonated capsule was supported on silica gel, which enabled adsorptive removal of stoichiometric fluoride from water.

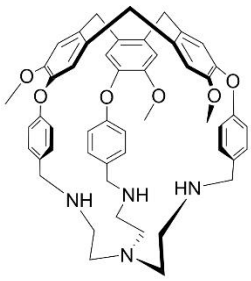


Figure 1

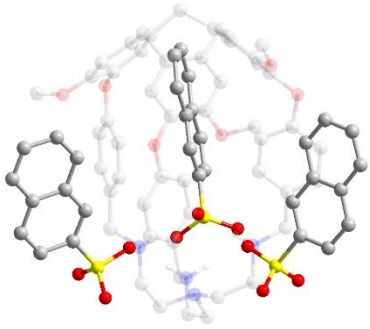


Figure 2

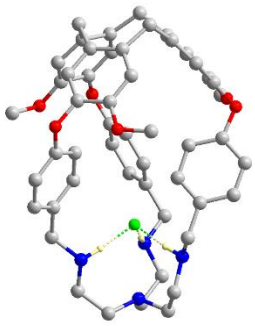


Figure 3

References

1. U. Darbost, M. N. Rager, S. Petit, I. Jabin, O. Reinaud, *J. Am. Chem. Soc.* **2005,** *127* (23), 8517–8525.
2. S. Le Gac, X. Zeng, C. Girardot, I. Jabin, *J. Org. Chem.* **2006,** *71* (24), 9233–9236.
3. Y. Lin, M. R. Gau, P. J. Carroll, I. J. Dmochowski, *J. Org. Chem.* **2022,** *87*, 5158–5165.

C7 The Therapeutic Potential of Supramolecular Self-associating Amphiphiles (SSAs)

Hiscock J.R.

School of Chemistry and Forensic Science, Ingram Building, University of Kent, UK, CT2 7NH.
E-mail: J.R.Hiscock@kent.ac.uk

Our novel patented (European Patent Application No. 18743767.8, U.S. Patent Application No. 16/632,194), Supramolecular Self-associating Amphiphile (SSA) platform technology currently contains a library of ≈ 120 molecules, with a structure related to the example shown in **Figure 1**. The anionic component of this class of compounds have been shown to self-associate through the formation of intermolecular hydrogen bonds creating (thio)urea-(thio)urea stacks, (thio)urea-anion tapes and (thio)urea-anion dimers, in the solid state, dependent on the counter cation present.

Further to this, within the solution state, members from this class of compound have been shown to retain the formation of anionic dimers in polar organic solvent. However, under aqueous conditions SSAs self-associate to form spherical aggregates commonly between 100 nm and 550 nm in diameter (**Figure 1**). In addition, the presence of inorganic salt causes these spherical aggregates to morph from sphere to fibre, producing a series of hydrogel materials.

Finally, this molecular technology has been shown to:

1. act as broad-spectrum antimicrobials;[1]
2. increase the efficacy of other antibiotic/antiseptic agents and anticancer agents against bacteria[2] and ovarian cancer cells respectively;[3]
3. selectively interact with phospholipid membranes of different compositions;[4]
4. have the potential to act as drug delivery vehicles.[5]

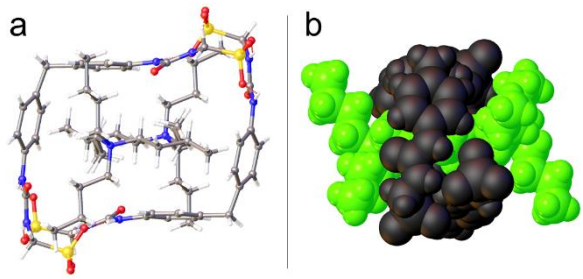


Figure 1. Single-crystal X-ray structure of a dianionic SSA, showing the formation of an intermolecular hydrogen bonded macrocycle illustrated as both (a) a ball and stick and, (b) a space filling model.

References

1. a) N. Allen, L. J. White, J. E. Boles, G. T. Williams, D. F. Chu, R. J. Ellaby, H. J. Shepherd, K. K. L. Ng, L. R. Blackholly, B. Wilson, D. P. Mulvihill, J. R. Hiscock, *ChemMedChem* **2020**, *15:22*, 2193; b) L. J. White, J. E. Boles, M. Clifford, B. Patenall, B., K. L. F. Hilton, K. K. L. Ng, R. J. Ellaby, C. K. Hind, D. P. Mulvihill, J. R. Hiscock, *Chem. Commun.* **2021**, *57*, 11839.
2. J. E. Boles, G. T. Williams, N. Allen, L. J. White, K. L. F. Hilton, P. I. A. Popoola, D. P. Mulvihill & J. R. Hiscock, *Adv. Therap.* **2022**, DOI: 10.1002/adtp.202200024.
3. N. O. Dora, E. Blackburn, J. E. Boles, G. T. Williams, L. J. White, S. E. G. Turner, J. D. Hothersall, T. Askwith, J. A. Doolan, D. P. Mulvihill, M. D. Garrett & J. R. Hiscock, *RSC Advances*, **2021**, *11*, 14213.
4. G. Townshend, G. S. Thompson, L. J. White, J. R. Hiscock & J. L. Ortega-Roldan, *Chem. Commun.* **2020**, *56*, 4015.
5. L. J. White, J. E. Boles, K. L. F. Hilton, R. J. Ellaby & J. R. Hiscock, *Molecules* **2020**, *25*, 4126.

C8 Fostering Host-Guest Sensing in Fluorescent Calixarene Scaffolds

Vigalok A.

School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel.
E-mail: avigal@tauex.tau.ac.il

Complexation of small organic and inorganic guests within the hydrophobic cavities of calixarene scaffolds has been known for many decades. Yet, translating such host-guest binding into the selective sensitive detection of important analytes remains a significant challenge. In recent years, we developed new synthetic strategies toward conjugated calixarene scaffolds that respond to the presence of such analytes by changing their fluorescent properties. A key feature of our design is the replacement of one of the oxygen atoms at the calixarene's lower rim with an aromatic acetylene moiety, which allows building extended fluorescent scaffolds with tunable properties (Figure 1).[1] In this presentation, I will discuss our latest results on the modifications of these scaffolds to prepare highly sensitive turn-off and ratiometric fluorescent probes that emit at long wavelengths, and respond to the presence of nitric oxide in aqueous solutions.

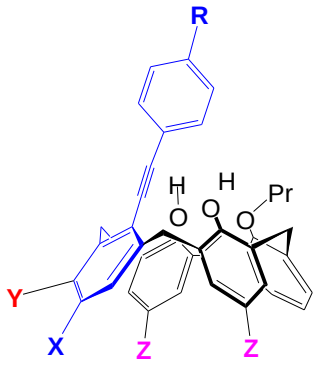


Figure 1.

References

1. a) B.B. Ahuja, A. Vigalok, *Angew. Chem. Int. Ed.* **2019**, *58*, 2774–2778; b) A. Baheti, R. Dobrovetsky, A. Vigalok, *Org. Lett*. **2020**, *22*, 9706–9711.

CDG From Heterocycles to Calixarenes: A Fascinating and Stimulating 45-Year Journey

de Mendoza J.

The Institute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans 16, 43007-Tarragona (Spain).

E-mail: jmendoza@iciq.es

Nowadays, calixarenes are worldwide recognized among the most useful and versatile building blocks to create molecular complexity. Unlike related bowl-shaped or cylindrical scaffolds (i.e. resorcinarenes, cavitands, pillarenes, cucurbiturils, cyclodextrins, cyclotriveratrylene, or coronarenes, among others), calixarenes simultaneously benefit from different sizes, shapes (conformations), controlled functionalization (at either upper and lower rims) and, most remarkably, a subtle balance between rigidity and flexibility, complexity and synthetic effort, which facilitates the design of novel chemical architectures for recognition, self-assembly, catalysis or material sciences.

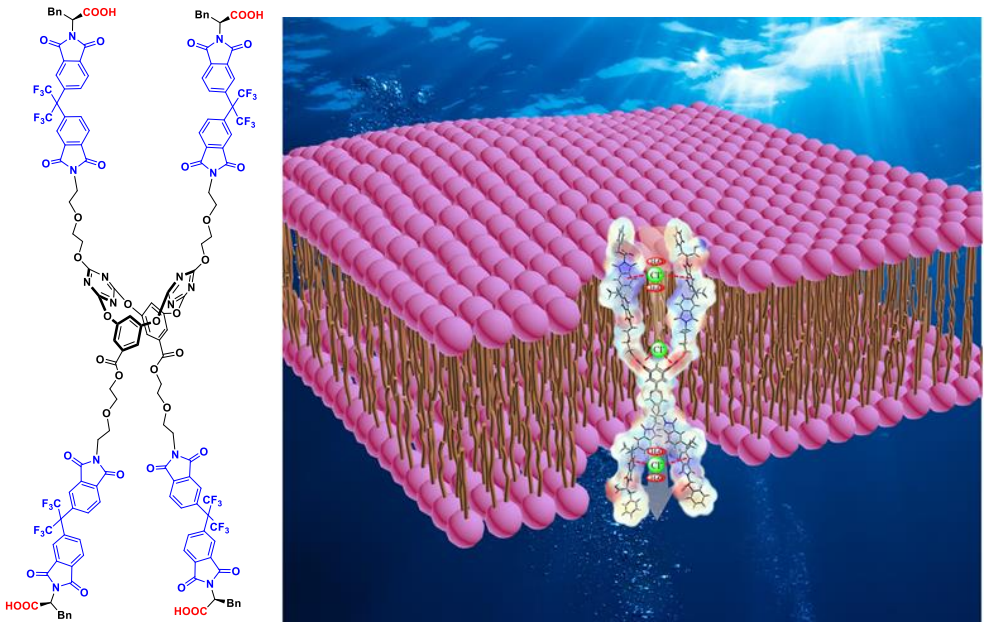
As a proud and grateful recipient of the fourth Award honoring the memory of C. David Gutsche, a truly visionary scientist on the future of these fascinating molecules and the father of the area for his pioneer work in their chemistry, following and rationalizing early steps on the condensation products of phenol with aldehydes, I want to dedicate this award lecture to Prof. Pilar Prados and also to many colleagues, co-workers and collaborators who made possible our contributions to the field for more than four decades. Without their inspiration and dedication, none of my contributions would have been possible.

C9 Oxacalix[2]arene[2]triazine-based Molecular Hourglass

Wang D.-X.

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China.
E-mail: dxwang@iccas.ac.cn

Chloride is the most abundant anion in nature. The transport of chloride across membranes is the basis of important physiological processes such as regulating electrical excitability, transepithelial transport, and cell volume.[1] Chloride transfer across the cell membrane is primarily mediated by ClC channels, which is believed that an hourglass-like pore formed with the two domain interfaces in the triangular ClC subunit center is responsible for chloride transfer.[2] Genetic defects in ClC channels could cause many severe diseases, including Bartter syndrome and Dent's disease.[1,2] It is anticipated that the preparation of a simple artificial molecule, which can mimic both the shape and function of the selective pore, would be one of the most interesting attempts. Presented here are artificial channel molecules that mimics the shape and function of the ClC channel selective pore. To facilitate the transport of chloride along a unimolecular pathway, anion-π interactions were introduced as the noncovalent driving force. The hourglass-like molecules were constructed with 1,3-alternate tetraoxacalix[2]arene[2]triazine as the narrowest (central) unit, two diglycolamine-linked imide arms were tethered as the extending part, and phenylalanine moieties were fixed as the terminal anchoring groups.[4] Anion/cation selectivity with permeability ratios $P_{Cl^-}/P_{K^+} \geq 1.90$ and anion/anion selectivity with $P_{Cl^-}/P_{Br^-} \geq 22.83$ were demonstrated.



References

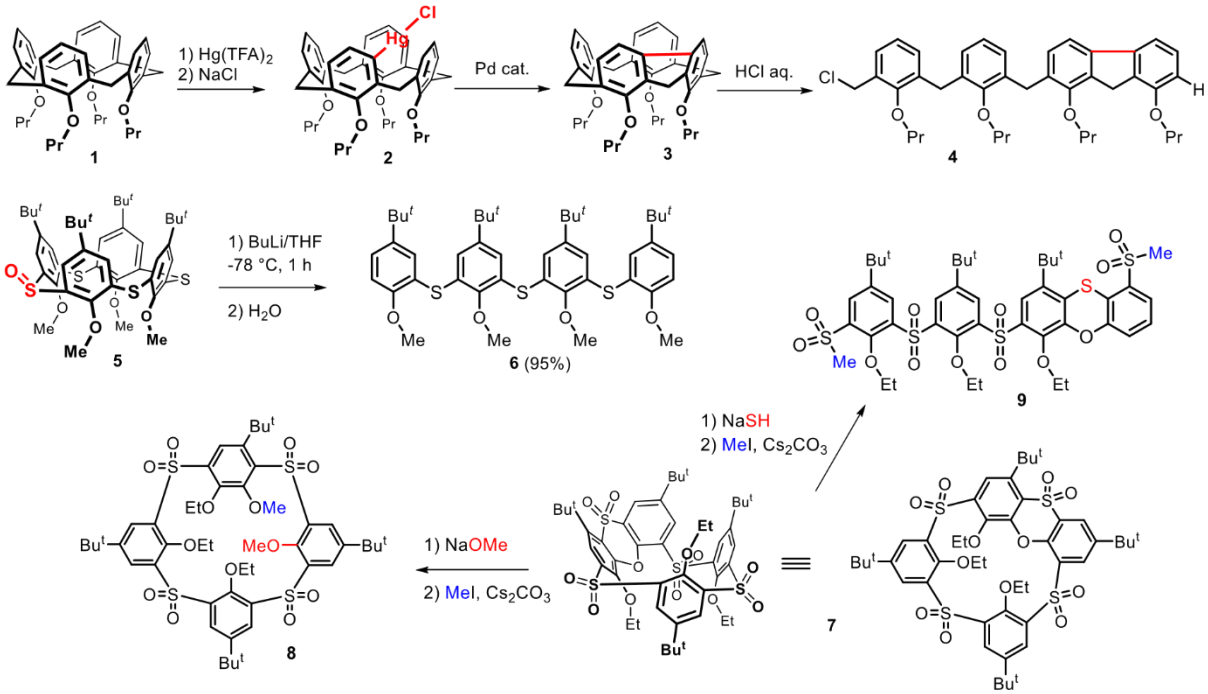
1. R. Dutzler, *FEBS Lett.* **2004**, *564*, 229-233.
2. R. Dutzler, E. B. Campbell, M. Cadene, B. T. Chait, R. MacKinnon, *Nature*, **2002**, *415*, 287-294.
3. W.-L. Huang, X.-D. Wang, Y.-F. Ao, Q.-Q. Wang, D.-X. Wang, *J. Am. Chem. Soc.* **2020**, *142*, 13273-13277.

C10 Unusual Reactivity of Macrocycles - How to Destroy Calixarenes?

Lhoták P.

Department of Organic Chemistry, University of Chemistry and Technology, Prague (UCTP), Technicka 5, 166 28 Prague 6, Czech Republic.
E-mail: lhotakp@vscht.cz

Contrary to calix[4]arenes with free OH functions, derivatives bearing alkoxy groups on the lower rim are usually considered to be very stable compounds as the macrocyclic skeletons are fully inert towards the action of both acidic and basic agents. The exception to this rule is represented by rigid highly strained calix[4]arene **3** which can be easily cleaved[1] to linear oligomer **4** (Scheme 1). Another exceptional reactivity was demonstrated on thiacalixarene sulfoxide **5**, which upon reaction wit BuLi provided linear tetramer **6** in essentially quantitative yield.[2] Moreover, as recently reported, the phenoxathiin-based thiacalixarene derivatives of type **7** undergo an unprecedented cleavage with RO^- providing a novel type of macrocycle **8** (Scheme 1),[3] comprising both calixarene and pillararene-like structural features (*meta*- and *para*-bridged phenolic units). Interestingly, cleavage with SH^- anion gave oligomer **9** through the rearrangement cascade of three S_NAr consecutive reactions.[4]



Scheme 1. All these reactions and their possible application in calixarene chemistry will be discussed.

References

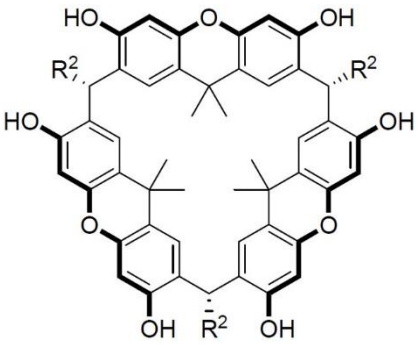
1. P. Slavik, H. Dvorakova, M. Krupicka, P. Lhotak, *Org. Biomol. Chem.* **2018**, *16*, 838-843.
2. J. Miksatko, V. Eigner, P. Lhotak, *RSC Advances*, **2017**, *7*, 53407-53414.
3. T. Landovsky, V. Eigner, M. Babor, M. Tichotova, H. Dvorakova, P. Lhotak, *Chem. Commun.* **2020**, *56*, 78-81.
4. T. Landovsky, M. Babor, J. Cejka, V. Eigner, H. Dvorakova, M. Krupicka, P. Lhotak, *Org. Biomol. Chem.* **2021**, *19*, 8075-8085.

I11 Synthesis and Application of Large and Conformationally Restricted Bowl-Shaped Macrocycles

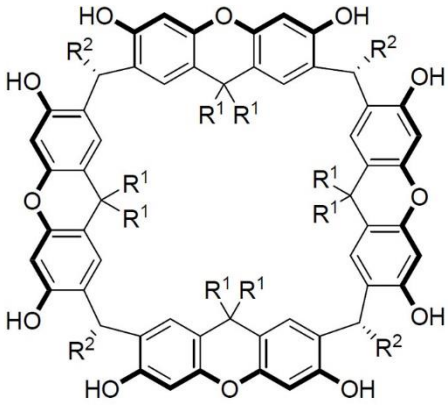
Tiefenbacher K.[a, b]

[a] Department of Chemistry, University of Basel, Mattenstrasse 24a, CH-4058 Basel, Switzerland; [b] Depart. of Biosystems Science and Eng., ETH Zürich, Mattenstrasse 26, CH-4058 Basel, Switzerland.
E-mail: konrad.tiefenbacher@unibas.ch , tkonrad@ethz.ch

Macrocycles are a cornerstone in supramolecular chemistry. A wide variety of macrocycles featuring different degrees of conformational freedom and sizes has been developed and explored intensively. An important subset of these macrocycles is comprised of conformationally restricted bowl-shaped derivatives, which are, for instance, required for the construction of cavitands[1] and also for the self-assembly of molecular capsules via non-covalent interactions.[2] The calixarene family of compounds, with the widely used member resorcin[4]arene is ideally suited for such purposes. Naturally, it was attempted to broaden this specific subclass of macrocycles by replacing the benzene-based building blocks with larger, for instance, naphthalene-derived ones. Unfortunately, attempts have failed to deliver size-extended conformationally restricted bowl-shaped resorcinarene-like macrocycles. My group recently reported the synthesis of such compounds, composed of three or four xanthene units, and proposed the name “xanthene[n]arenes” (**X-n**). We demonstrated that they are well suited for the construction of deeper cavitands, hydrocarbon belts, and the self-assembly of hydrogen bond-based molecular capsules. The latest, unpublished results concerning these studies will be presented.



xanthene[3]arene (**X-3**)



xanthene[4]arenes (**X-4**)

References

1. a) D. J. Cram, *Science* **1983,** *219*, 1177-1183; b) S. M. Biros, J. Rebek, *Chem. Soc. Rev.* **2007,** *36*, 93-104.
2. M. M. Conn, J. Rebek, *Chem. Rev.* **1997,** *97*, 1647-1668.
3. J. Pfeuffer-Rooschüz, L. Schmid, A. Prescimone, K. Tiefenbacher, *JACS Au* **2021**, *11*, 1885–1891.

C11 Calixarene-Mediated Protein Assembly and Encapsulation

Crowley P. B.

School of Biological and Chemical Sciences, University of Galway, Ireland.
E-mail: peter.crowley@nuigalway.ie

A myriad of methods is in development to address the protein assembly challenge.[1] One approach relies on water-soluble calixarenes that bind simultaneously to two or more protein surfaces.[2-4] Recent work with sulfonato-calix[8]arene (**sclx$_8$**) and cytochrome *c*[2] or the lectin RSL[3] has revealed the possibility of macrocycle-mediated protein frameworks (Figure 1). These highly porous structures have features that may suit the design of new biomaterials. In addition, the crystal structures reveal the possibility of protein encapsulation by calix[8]arene.

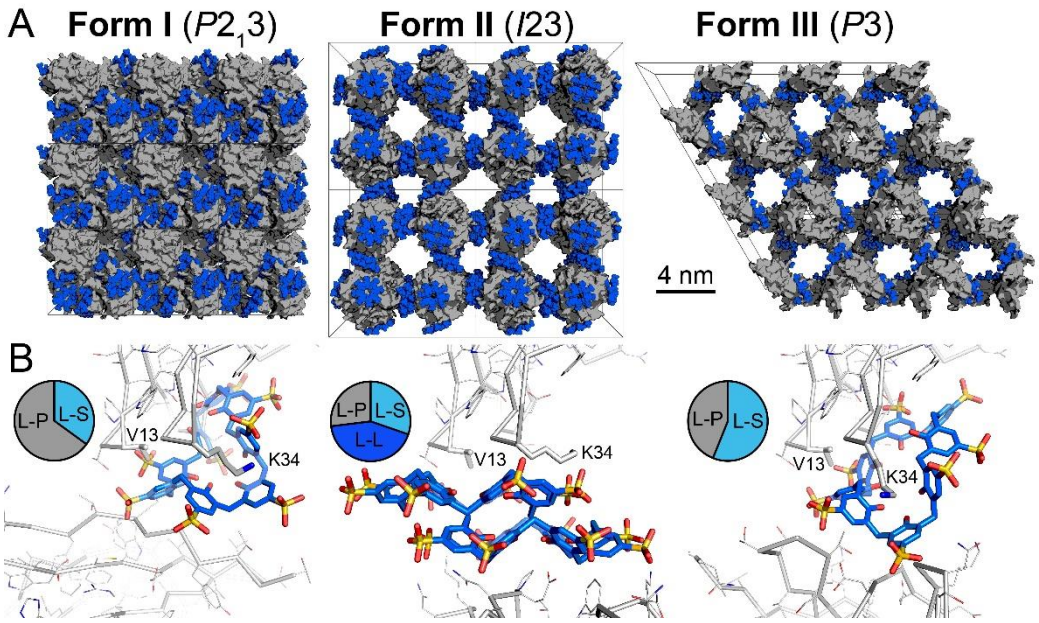


Figure 1. **(A)** Crystal packing in RSL-**sclx$_8$** co-crystal forms I-III. Protein shown as grey surfaces and **sclx$_8$** shown as blue spheres. Note the nanometer-scale solvent channels in forms II and III.[3] **(B)** Details of the principal protein-**sclx$_8$**-protein interfaces in each crystal form. Pie charts show area proportions of **sclx$_8$**-mediated interfaces. L; ligand, P; protein, S; solvent.

References

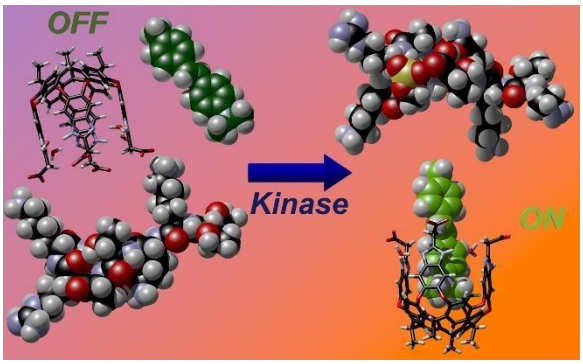
1. J. Zhu, N. Avakyan, A. Kakkis, A. M. Hoffnagle, K. Han, Y. Li, Z. Zhang, T. Su Choi, Y. Na, C.-J. Yu, F. A. Tezcan, *Chem. Rev.* **2021**, *121*, 13701–13796.
2. S. Engilberge, M. L. Rennie, E. Dumont, P. B. Crowley, *ACS Nano* **2019**, *13*, 10343-10350.
3. K. O. Ramberg, S. Engilberge, T. Skorek, P. B. Crowley, *J. Am. Chem. Soc.* **2021**, *143*, 1896-1907.
4. P. B. Crowley, *Acc. Chem. Res.* **2022**, In the press, 10.1021/acs.accounts.2c00206

C12 Biosensing with Water-Soluble Deep Cavitands

Hooley R. J.

Department of Chemistry; University of California-Riverside, Riverside, CA, 92521, U.S.A.
E-mail: richard.hooley@ucr.edu

Variably functionalized self-folding deep cavitands form an arrayed, fluorescent indicator displacement assay system for the detection of a variety of biomolecules, from steroids[1] and drugs of abuse[1] to post-translationally modified (PTM) peptides[2] and nucleotides[3,4] in multiple types of biological media. Multiple recognition mechanisms can be exploited, either direct cavity-based binding of species such as trimethyllysine (KMe_3), or indirect charge-based recognition of differentially functionalized peptides or non-canonically folded oligonucleotides. These multiple sensing mechanisms allow highly sensitive discrimination between miniscule differences in target structures. The host arrays can be coupled to a fluorescence-based supramolecular tandem assay that allows site-selective *in situ* monitoring of post-translational modifications catalyzed by different types of enzymes including lysine methyltransferases and demethylases, as well as phosphatases or kinases. The synergistic application of multiple variables in a single arrayed sensor system allows dual-mode deep cavitands to approach levels of recognition selectivity usually only seen with antibodies.



References

1. A.D. Gill, B.L. Hickey, W. Zhong, R.J. Hooley, *Chem. Commun.* **2020**, *56*, 4352–4355.
2. Y. Liu, J. Lee, L. Perez, A.D. Gill, R.J. Hooley, W. Zhong, *J. Am. Chem. Soc.* **2018**, *140*, 13869–13877.
3. J. Chen, B.L. Hickey, L. Wang, J. Lee, A.D. Gill, A. Favero, R. Pinalli, E. Dalcanale, R.J. Hooley, W. Zhong, *Nat. Chem.* **2021**, *13*, 488–495.
4. J. Chen, A.D. Gill, B.L. Hickey, Z. Gao, X. Cui, R.J. Hooley, W. Zhong, *J. Am. Chem. Soc.* **2021**, *143*, 12791–12799.

C13 Minimal Protein Affinity Tags

Urbach A. R.

Department of Chemistry, Trinity University, San Antonio, TX, 78212.
E-mail: aurbach@trinity.edu

The molecular recognition of polypeptides by synthetic compounds drives many areas of contemporary science and technology. We are focused on developing approaches by which polypeptides can be targeted predictively on the basis of the sequence of amino acids. Studies using cucurbit[n]uril synthetic receptors have enabled the binding of N-terminal and non-terminal sites on polypeptides in neutral aqueous solution and with equilibrium dissociation constant values in the nanomolar to micromolar range in neutral aqueous buffer. This brief presentation will describe the lessons learned from these studies since this investigator's last presentation to this forum, and the resulting applications as minimally sized protein affinity tags.

C14 Design and Synthesis of Cyclic Nucleobase as a New Scaffold for Molecular Recognition and Ion Separation

Shi X.

Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, Tampa, Florida 33620, USA.

E-mail: xmshi@usf.edu

Guanosine with 2-amino and 6-carbonyl groups as a hydrogen bond donor and receptor can assemble into a unique G_4-quartet building block through ion-dipole interactions between the central oxygens and cations. In many cases, G-quadruplexes formed from the stacking of G_4-quartet and the assembly of a specific and stable G-quadruplex in H-bond competitive solvents remains a challenging task. Herein, with the modification on both guanine (8-aryl) and ribose (sterically hindered 2', 3'position), a concise and well-defined bottom-to-bottom stacking G_8-octamer was formed with a metal template in solution. K^+ complexes showed an excellent binding affinity over Ba^{2+}, which explained the observed super good K^+ selectivity even over the well-known potassium 18-crown-6, indicating the potential potassium receptor. The meta position of the two phenyl groups on the C-8 position could further construct cross-layer covalent linkers. The covalently tethered 8-aryl G_8-octamer remains intact in protic solvent CD_3OD and even showed significantly improved stability in 1:1 DMSO/$CDCl_3$ mixture, which demonstrates the significantly enhanced stability of G-quadruplexes. To the best of our knowledge, this is one of the few stable G-quadruplex systems from small molecule self-assembly to survive in a H bond competitive environment. Isoguanosine (isoG, also known as 2-hydroxy-adenosine) is a structural isomer of guanosine. The self-assembled pentaplexes are excellent Cs^+ selective ionophores even in the presence of excess alkali cations. To avoid the dynamic equilibrium of individual isoG subunits in solution, the post-assembly modification of a cation templated isoG complex with the subsequent formation of a Cs cation ionophores was described. Reversible olefin metathesis is used to cross-link subunits within an isoG pentaplex constructing cyclic pentamer. The covalent tethered isoG oligomer formed in this way can be used to extract Cesium cation from an aqueous source into an organic receiving phase. The oligomer can be recycled and proved more effective as an extractant than the corresponding free monomer. The results clearly demonstrate the power of covalent tethered molecular self-assembly for the construction of highly selective ionophores. The successful synthesis and study of these covalent tethered cyclic complexes based on the supramolecular template are very promising building blocks in chemical, material, and medicinal research.

References

1. Y. He, Y. Zhang, L. Wojtas, N. G. Akhmedov, D. Thai, H. Wang, X. Li, H. Guo, X. Shi, *Chem. Sci.* **2019***, 10*, 4192-4199.
2. Y. He, Y. Zhang, L. Wojtas, N. Akhmedov, Q. Pan, H. Guo, X. Shi, *Chem. Asian J.* **2020**, *15*, 1030-1034.
3. Y. Zhang, Y. He, L. Wojtas, X. Shi, H. Guo, *Cell Rep. Phys. Sci.* **2020**, *1*, 100211.
4. M. Liu, Y. He, C. Shan, L. Wojtas, I. Ghiviriga, O. Fathalla, Y. Yan, X. Li, X. Shi, *Chem. Sci.* **2021**, *12,* 7569-7574.
5. Y. He, Y. Zhang, M. Liu, K. Zhao, C. Shan, L. Wojtas, H. Guo, A. Ding, X. Shi, *Cell Rep. Phys. Sci.* **2021**, *2*, 100519.
6. Y. He, M. Liu, S. Teng, L. Wojtas, G. Gu, X. Shi, *Chin. Chem. Lett.* **2022**, 03, 007.

I12 Activating and Monitoring Membrane Transport with Macrocycles

Nau W.M.

School of Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany
E-mail: w.nau@jacobs-university.de

Water-soluble macrocycles such as *p*-sulfonatocalixarenes, cyclodextrins, and cucurbiturils can be used for the temporally and spatially resolved monitoring of membrane transport processes.[1] The underlying idea is that a macrocyclic receptor is encapsulated along with a binding fluorescent dye in the interior of liposomes or cells, such that a binding analyte that crosses the lipid bilayer membrane complexes with the macrocycle, displaces the fluorescent dye, and causes a characteristic fluorescence response which can be directly related to the transport kinetics, see Fig. 1.
In an orthogonal line of applications, macrocycles of the amphiphilic type can also be used to transport otherwise impermeable cargo molecules through the lipid bilayer membrane, see Fig. 1. This allows the pairing of different macrocycles, one for chemosensing and one for membrane transporting, to develop refined functional networks based on supramolecular chemistry principles.[2]

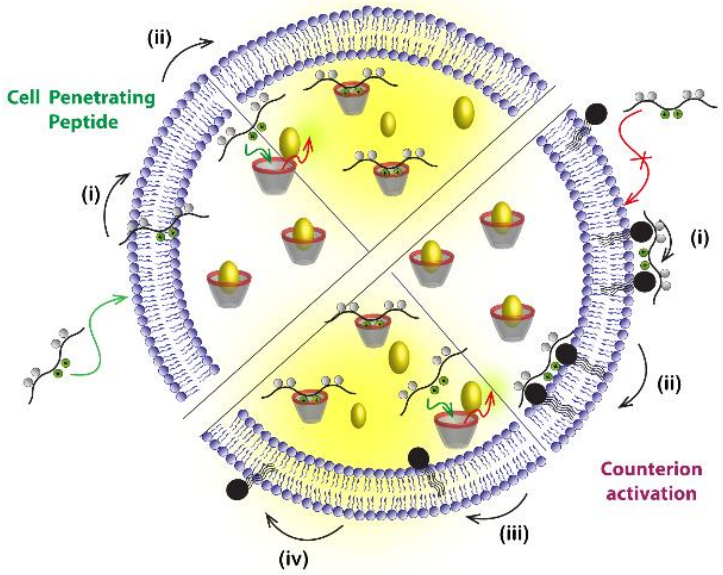


Figure 1. Strategy for using supramolecular membrane transport assays to detect direct (left and top quadrant) or macrocyclic carrier-assisted (right and bottom quadrant) peptide transport.

References

1. a) G. Ghale, A. G. Lanctôt, H. T. Kreissl, M. H. Jacob, H. Weingart, M. Winterhalter, W. M. Nau, *Angew. Chem. Int. Ed.* **2014**, *53*, 2762–2765. b) A. Norouzy, Z. Azizi, W. M. Nau, *Angew. Chem. Int. Ed*. **2015**, *54*, 792–795. c) K. I. Assaf, B. Begaj, A. Frank, M. Nilam, A. Mougharbel, U. Kortz, J. Nekvinda, B. Gruner, D. Gabel, W. M. Nau, *J. Org. Chem.* **2019**, *84*, 11790–11798. d) F. Biedermann, G. Ghale, A. Hennig, W. M. Nau, *Communic. Biol.* **2020**, *3*, 383. e) S. He, A. Zhiti, A. Barba-Bon, A. Hennig, W. M. Nau, *Fontiers Chem.* **2020**, *8*, 597927. f) M. Nilam, S. Collin, S. Karmacharya, A. Hennig, W. M. Nau, *ACS Sensors* **2021**, *6*, 175–182. g) S. Pangeni, J. Prajapati, B. Dahyabhai, A. Jayesh, N. Mohamed, W. M. Nau, U. Kleinekathöfer, M. Winterhalter, *Angew. Chem. Int. Ed.* **2021**, *60*, 8089–8094.
2. a) S. Peng, A. Barba-Bon, Y.-C. Pan, W. M. Nau, D.-S. Guo, A. Hennig, *Angew. Chem. Int. Ed*. **2017**, *56*, 15742–15745. b) Y.-C. Pan, A. Barba-Bon, H. W. Tian, F. Ding, A. Hennig, W. M. Nau, D. S. Guo, *Angew. Chem. Int. Ed.* **2021**, *60*, 1875–1882. c) A. Barba-Bon, Y.-C. Pan, F. Biedermann, D.-S. Guo, W. M. Nau, A. Hennig, *J. Am. Chem. Soc.* **2019**, *141*, 20137–20145. d) A. Barba-Bon, G. Salluce, I. Lostalé-Seijo, K. I. Assaf, A. Hennig, J. Montenegro, W. M. Nau, *Nature* **2022**, *603*, 637–642.

I13 Pillar[n]MaxQ: Synthesis, Molecular Recognition Properties, and *In Vivo* Sequestration Processes

Isaacs L.,[a] Xue W.,[a] Deng C.,[a] Zhai C.,[a] Zavalij P.,[a] Brockett A.,[c] Shuster M.,[b] Briken V.,[b] Roesch M. R.[c]

[a] Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, United States; [b] Department of Cell Biology and Molecular Genetics, University of Maryland, College Park, MD 20742, United States; [c] Department of Psychology, University of Maryland, College Park, MD 20742, United States.

E-mail: LIsaacs@umd.edu

In this presentation, I describe the thought process that lead us from ultratight CB[n]•guest complexes to the design and synthesis of a new class of ultrahigh affinity pillararene hosts dubbed Pillar[n]MaxQ (K_a up to 10^{12} M^{-1} in phosphate buffered water). Pillar[n]MaxQ bind substantially more tightly toward their guests than the analogous pillararenes featuring OCH_2CO_2H groups. Pillar[n]MaxQ selectively bind hydrophobic **Q**uaternary ammonium ions in preference to hydrophobic primary ammonium ions. Pillar[6]MaxQ binds to biologically and medicinally important guest compounds like neuromuscular blockers (rocuronium, vecuronium) and drugs of abuse with high affinity. *In vitro* cytoxicity assays for Pillar[6]MaxQ performed with kidney and liver cells indicate good compatibility up to 100 µM whereas an *in vivo* (Swiss Webster mice) maximum tolerated dose study showed that Pillar[6]MaxQ is well tolerated up to 40 mg/kg. Pillar[6]MaxQ does not inhibit the hERG ion channel and is not mutagenic according to the Ames fluctuation test. Finally, we perform open-field tests to quantify locomotor activity of animals treated with methamphetamine or fentanyl followed by Pillar[6]MaxQ as supramolecular antidote.

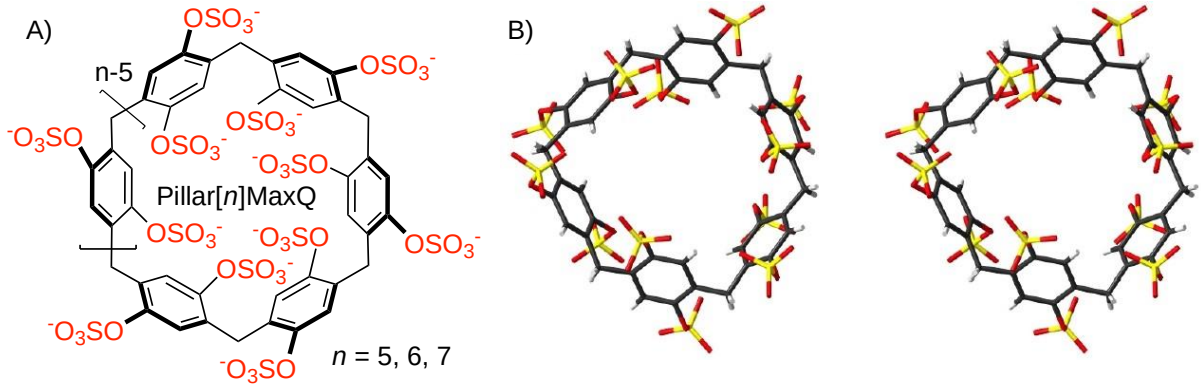


Figure 1. A) Chemical structure and B) Cross-eyed stereoview of Pillar[6]MaxQ in the crystal.

References

1. W. Xue, P. Y. Zavalij, L. Isaacs, *Angew. Chem. Int. Ed.* **2020**, *59*, 13312-13319.

I14 Probing the Self-Assembly Behavior of Tubular Macrocycles

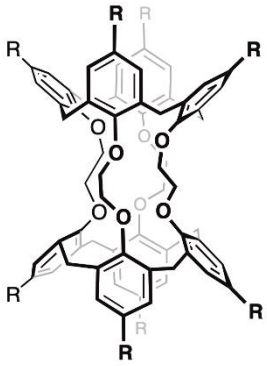
Parisi M.F.

Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, viale F. Stagno d'Alcontres 31, 98166 Messina, Italy.

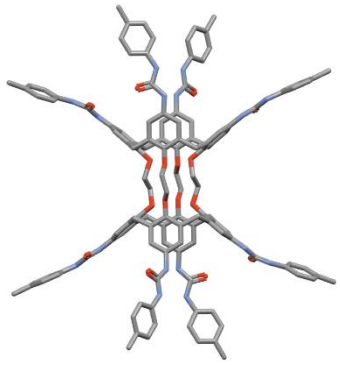
E-mail: mparisi@unime.it

Calix[4]tubes **1** are tubular molecules consisting of two calix[4]arene units linked, at their narrow rims, by four ethylene bridges. The latter, together with the macrocyclic phenolic oxygen atoms, create a cryptand-like binding site that encapsulates potassium ions with remarkable selectivity.[1] To date, calix[4]tube derivatization[2] has mostly focused on the substitution pattern at the wide rims so as to modulate and control the ionophoric properties, whereas the design of calix[4]tube-based building blocks capable of undergoing self-assembly or formation of supramolecular arrays has not really been explored.

To shed light on the full supramolecular potential of this class of compounds we have recently synthesized[3] octa-aminocalix[4]tube **2a** and its octa-tolylurea derivative **2b** and, in the course of this presentation, I will comment on the fine-tuning of the self-assembly of these derivatives both in solution and in the solid state.



1: R = *t*-Bu; H, *t*-Oct
2a: R = NH_2
2b: R = NHCONHTol



Solid-state structure of **2b**

References

1. a) P. Schmitt, P. D. Beer, M. G. B. Drew, P. D. Sheen, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1840–1842; b) S. E. Matthews, P. Schmitt, V. Felix, M. G. B. Drew, P. D. Beer, *J. Am. Chem. Soc.* **2002**, *124*, 1341–1353.
2. a) S. E. Matthews, P. D. Beer, in Calixarenes in the Nanoworld (Eds: Vicens, J., Harrowfield, J., Baklouti, L.) Spriger, Dordrecht **2007**, Ch. 6; b) K. Puchnin, P. Zaikin, D. Cheshkov, I. Vatsouro, V. Kovalev, *Chem. Eur. J.* **2012**, *18*, 10954–10968.
3. M. Gaeta, E. Rodolico, M. E. Fragalà, A. Pappalardo, I. Pisagatti, G. Gattuso, A. Notti, M. F. Parisi, R. Purrello, A. D'Urso, *Molecules* **2021**, *26*, 704.

I15 Molecular Baskets

Badjić J.D.

Department of Chemistry & Biochemistry, The Ohio State University, 100 West 18th Avenue, Columbus OH 43210.
E-mail: badjic.1@osu.edu

Molecular baskets with amino acids at their rim[1] can be made to trap nerve agents, toxic compounds, and anticancer drugs in water (Figure 1). In one instance, photo-induced decarboxylation of baskets holding glycine reduces their solubility to lead to precipitation of OP nerve agent or anticancer drug occupying the cavity.[2] The process is simple, facile, effective and could amount to a novel method for removing minute quantities of targeted substances from aqueous systems. Potential applications in the areas of environmental chemistry, drug purification and/or sequestration of toxic compounds from biological systems come to mind. In another instance, the irradiation of a basket containing three glutamic acids at its rim causes the exclusive removal of a-carboxylic groups while g-carboxylates remain intact.[3] The chemical change triggers aggregation and assembly of now amphiphilic hosts into nanoparticles. With our recent efforts centered on developing molecular baskets and their assemblies into sequestering agents capable of safe removal of fentanyl or toxic anticancer drugs from biological systems, my lecture will describe discoveries related to the preparation of these cavitands[4] and their use for creating covalent dissipating cages for spatiotemporal control of the sequestration.

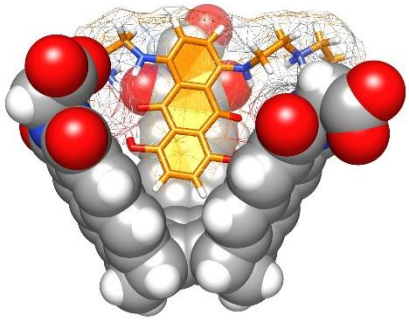


Figure 1. A CPK representation of molecular basket with Gly at top and anticancer drug mitoxantrone occupying the cavity.

References

1. T. J. Finnegan, V. W. L. Gunawardana, J. D. Badjic, *Chemistry A European Journal* **2021**, *27*, 13280-13305.
2. S. E. Border, R. Z. Pavlovic, L. Zhiquan, J. D. Badjic, *Journal of the American Chemical Society* **2017**, *139*, 18496-18499.
3. R. Z. Pavlovic, S. E. Border, Y. Li, X. Li, J. D. Badjic, *Chemical Communications* **2020**, *56*, 2987-2990.
4. M. J. Gunther, R. Z. Pavlovic, T. J. Finnegan, X. Wang, J. D. Badjic, *Angewandte Chemie, International*
5. *Edition* **2021**, *60*, 25075-25081.

I16 Triazole Scaffold Calix[n]arenes

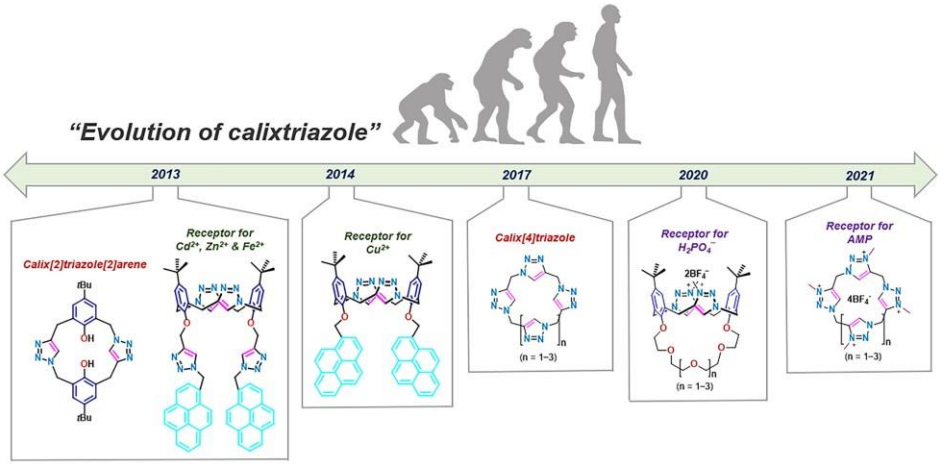
Kim J.S.,[a] Cho J.,[b] Kim S.[b]

[a] *Department of Chemistry, Korea University, Seoul 02841, Korea;* [b] *College of Pharmacy, Seoul National University, Seoul 08826, Korea.*

E-mail: jongskim@korea.ac.kr

Macrocyclic host molecules contain a variety of supramolecular receptors with cyclic structures. Most of the reported macrocyclic host molecules consist of repeating building blocks that determine the structural properties and recognition capacity. With this in mind, a series of 1,2,3-triazole framed calixarenes have been designed and synthesized. In 2013, our group first synthesized calix[2]triazole[2]arene,[1] a novel heterocalixarene consisting of two phenol groups and two 1,2,3-triazole moieties. The selective recognition ability of calix[2]triazole[2]arene for specific cations was demonstrated through the fluorescence change of the appended pyrene group.

Pyrenyl-appended calix[2]triazole[2]arene containing a 1,2,3-triazole linker exhibited bimodal sensing ability for Zn^{2+} (or Cd^{2+}) and Fe^{2+} through increased monomer and excimer emission,[2] and pyrenyl-appended calix[2]triazole[2]arene containing an ether linker exhibited excellent selectivity for Cu^{2+} through pyrenyl excimer emission change.[3,4,5] In addition, calix[n]triazoliums were synthesized through methylation of calix[n]triazoles in order to apply calix[n]triazoles to anion binding studies.[6] It was found that calix[n]triazoliums selectively recognized only adenosine 5'-monophosphate (AMP) compared to various anions including polyphosphate through the remarkable fluorescence enhancement by indicator displacement assay (IDA) using chromenolate anion. Currently, various types of calixtriazole derivatives are being synthesized, and studies using them are actively conducted. This young heterocalixarene opens up new possibilities as an attractive molecular platform in the field of supramolecular chemistry.



References

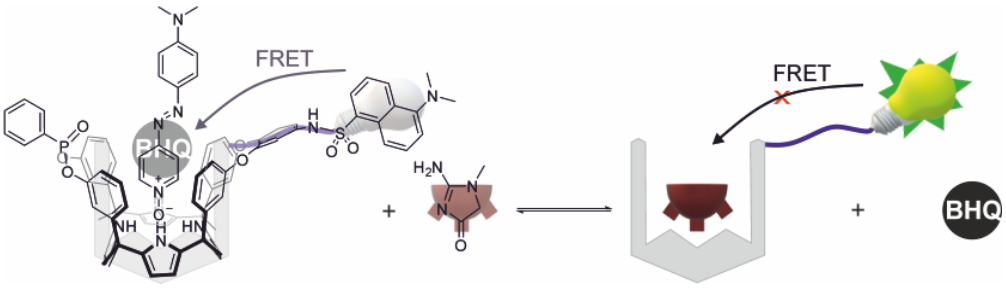
1. J. Cho, S. Lee, S. Hwang, S. H. Kim, J. S. Kim, S. Kim, *Eur. J. Org. Chem.* **2013**, 4614-4623.
2. J. Cho, T. Pradhan, J. S. Kim, S. Kim, *Org. Lett.* **2013**, *15*, 4058-4061.
3. J. Cho, T. Pradhan, Y. M. Lee, J. S. Kim, S. Kim, *Dalton Trans.* **2014**, *43*, 16178-16182.
4. J. Cho, P. Verwilst, M. Kang, J.-L. Pan, A. Sharma, C. S. Hong, J. S. Kim, S. Kim, *Chem. Commun*. **2020**, *56*, 1038-1041.
5. I. Kim, K. C. Ko, W. R. Lee, J. Cho, J. H. Moon, D. Moon, A. Sharma, J. Y. Lee, J. S. Kim, S. Kim, *Org. Lett.* **2017**, *19*, 5509-5512.
6. J. Cho, J. Shin, M. Kang, P. Verwilst, C. Lim, H. Yoo, J. G. Kim, X. Zhang, C. S. Hong, J. S. Kim, S. Kim, *Chem. Commun.* **2021**, *57*, 12139-12142.

I17 Supramolecular Recognition and Sensing of Creatinine Using Phosphonate Aryl-Extended Calix[4]pyrrole Cavitands

Ballester P.[a,b]

[a] ICREA, Passeig Lluís Companys 23, 08018 Barcelona, Spain; [b] Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology (BIST), Avgda. Països Catalans 16, 43007 Tarragona, Spain.
E-mail: pballester@iciq.es

In this presentation, I will describe a synthetic receptor, an aryl-substituted calix[4]pyrrole with a monophosphonate bridge, that displays remarkable affinity for creatinine and the creatininium cation. The receptor works by including the guest in its deep and polar aromatic cavity and establishing directional interactions in three dimensions. When incorporated into a suitable polymeric membrane, this molecule acts as an ionophore allowing the development of a highly sensitive, ion-selective potentiometric sensor suitable for the determination of creatinine levels in biological fluids, such as urine or plasma, in an accurate, fast, simple, and cost-effective.[1] I will also describe our efforts in using the synthesized receptor for the design of supramolecular fluorescent sensors for creatinine and its lipophilic derivative hexylcreatinine. To this end, we used indicator displacement assays (IDAS) of an inherently fluorescent guest dye or a black-hole quencher from the receptor's cavity by means of competition with the creatinine analytes. For the use of the black-hole indicator dye, the receptor's calix[4]pyrrole scaffold was modified with a dansyl chromophore as a signalling unit that engages in Förster resonance energy transfer with the indicator dye. The competitive displacement of the indicators by hexylcreatinine produced supramolecular fluorescence turn-on sensors that work at micromolar analyte concentrations.[2]



References

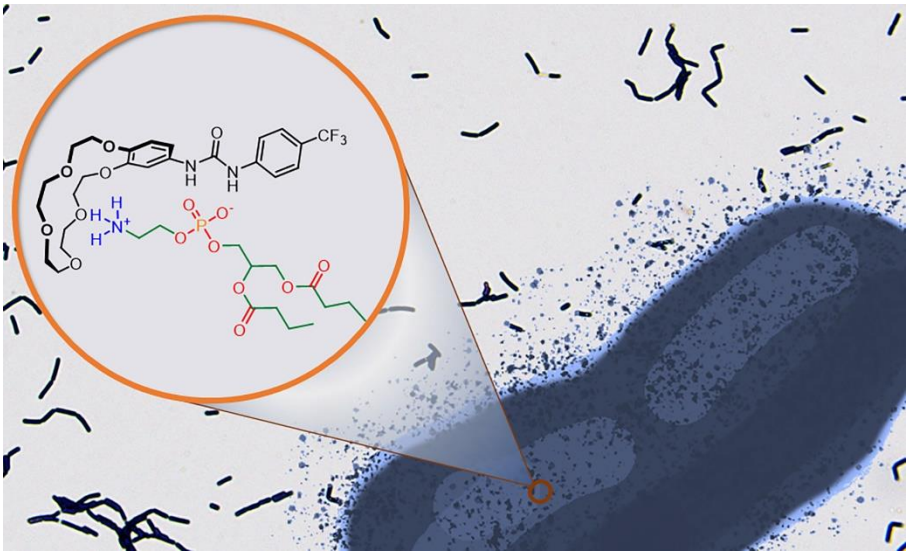
1. a) T. Guinovart, D. Hernandez-Alonso, L. Adriaenssens, P. Blondeau, M. Martinez-Belmonte, F.X. Rius, F.J. Andrade, P. Ballester, *Angew. Chem., Int. Ed.* **2016**, *55*, 2435-244; b) A. Corba, A.F. Sierra, P. Blondeau, B. Giussani, J. Riu, P. Ballester, F.J. Andrade, *Talanta* **2022**, 123473.
2. a) A.F. Sierra, D. Hernández-Alonso, M.A. Romero, J.A. González-Delgado, U. Pischel, P. Ballester, *J. Am. Chem. Soc.* **2020**, *142*, 4276-4284; b) A.F. Sierra, G. Aragay, G. Peñuelas-Haro, P. Ballester, *Org. Chem. Front.* **2021**, *8*, 2402-2412

C15 Supramolecular Hosts Targeting Bacterial Phospholipids

Busschaert N.

Department of Chemistry, Tulane University, New Orleans, LA, United States.
E-mail: nbusschaert@tulane.edu

An estimated 2.8 million people are infected each year in the United States with antibiotic-resistant bacteria, and more than 35,000 people die as a result.[1] The rise in antibiotic-resistance is due to a combination of the overuse and misuse of antibiotics, as well as the innate ability of bacteria to develop resistance against antibacterial agents. There is therefore a constant need to develop new antibiotics to ensure that there are alternative treatment options. One target that is often considered to be less prone to resistance mechanisms, is the bacterial membrane. Resistance is thought to be less likely due to the rapid bactericidal effect of membrane disruption, and the fact that lipid mutations are less trivial than protein mutations.[2] Furthermore, membrane-active agents do not have to cross the membrane and enter the bacterial cell, thereby avoiding problems due to efflux pumps. We have thus developed a range of supramolecular hosts that can bind to the head group of bacterial lipids such as phosphatidylethanolamine (PE)[3] and phosphatidylglycerol (PG)[4]. ^{1}H NMR studies in organic solutions and liposome-based assays confirmed that our hosts selectively bind to these bacterial lipids over the mammalian lipid phosphatidylcholine (PC). The best lipid-binding hosts also display antibacterial activity against a range of Gram-positive bacteria, such as *B. subtilis*, *S. aureus* and *E. faecalis*, with minimum inhibitory concentrations (MICs) close to those of natural membrane-acting antimicrobial peptides (MICs 25-50 μM). Mode-of-action studies further confirmed that the antibacterial activity of the lipid hosts is due to a membrane-related mechanism.



References

1. Centers for Disease Control and Prevention (CDC), *Antibiotic resistance threats in the United States*, Atlanta, GA, **2019**.
2. M. Zasloff, *Nature* **2002**, *415*, 389.
3. S. R. Herschede, H. Gneid, T. Dent, E. B. Jaeger, L. B. Lawson, N. Busschaert, *Org. Biomol. Chem.* **2021**, *19*, 3838-3843.
4. E. S. Williams, H. Gneid, S. R. Marshall, M. J. González, J. A. Mandelbaum, N. Busschaert, *Org. Biomol. Chem.* **2022**.

I18 SAR in the Anti-Biofilm Activity of Cationic Pillararenes and the Use of Pillararene Derivatives as Scaffolds for the Preparation of Supramolecular Boxes

Cohen Y.

School of Chemistry, Faculty od Exact Science, Tel Aviv University, Ramat Aviv 6977801, Tel Aviv, Israel.

E-mail: ycohen@tauex.tau.ac.il

Pillararenes, first synthesized in 2008,[1] have been used in myriad applications in different research fields.[2] For example we have shown that pillararene derivatives can be used as host for Xenon in water and as scaffolds for supramolecular organogels.[3] We also demonstrated that cationic pillararenes are, non-hemolytic, potent inhibitors of biofilm formation in Gram positive bacteria.[4a,b] In the lecture we will present some of our recent results regarding the structure activity relationship (SAR) of these cationic pillararenes. In this study we show that that a plurality of accessible positive charges is needed for the observed activity. The nature of the positive charges and the cavity of the pillararene appear not to have an effect on the observed biological activity.[4c] These inhibitors of biofilm formation were found to be non-hemolytic and show no effect on cell viability of human and bacterial cells.[4c]
Molecular containers, which can isolate molecular species from the bulk, may, in principle, be used as nano-flasks and as drug delivery systems. Recently we could show that that per-diethyl- amino-pillar[6]arene forms with mellitic acid supramolecular hexagonal boxes (SHBs).[5a] These water-soluble SHBs, which are based on charge assist-hydrogen bonds, were characterized by NMR, DOSY, MS and computational methods and were found to be pH-responsive. Very recently, we prepared supramolecular pentagonal boxes (SPBs) based on pillar[5]arene derivatives[5b] showing quite different characteristics as compared to SHBs. If time will permit, we will provide evidence for the formation of such extend supramolecular boxes in water.

References

1. a) T. Ogoshi, et al., *J. Am. Chem. Soc*., **2008**, *130*, 5022-5023; b) T. Ogoshi, et al., *Chem. Rev.*, **2016**, *116*, 7937–8002.
2. a) K. Kato et al., *Chem. Soc. Rev*., **2022**, 10.1039/d2cs00169a; b) Y. T. Li, et al., *ACS Sensors*, **2021**, *6*, 3882-3897; c) M. H. Lou, et al., *Chem. Commun*., **2021**, *57*, 13429-13447; d) K. Y. Wang, et al., *Angew. Chem. Int. Ed*., **2021**, *60*, 8205-9214; e) T. Ogoshi, et al., *Angew. Chem. Int. Ed*., **2019**, *58*, 2187-2206; f) N. Song, et al., *Theranostics*, **2019**, *9*, 3075-3093.
3. a) T. Adiri et al., *Chem. Commun.,* **2013**, *49*, 7082-7084; b) Y. Zafrani, et al., *Chem. Eur. J*., **2018**, *25*, 15750-15755; c) D. Kaizerman-Kane, et al., *Org. Chem. Front.,* **2019**, *6*, 3348-3354.
4. a) R. Joseph, et al., *J. Am. Chem. Soc*., **2016**, *138*, 754-757; b) R. Joseph, et al., *Chem. Commun.,* **2016**, *52*, 10656-10659; c) D. Kaizerman-Kane, et al., *ACS Infec. Dis*., **2021**, 7, 579-585.
5. a) D. Kaizerman-Kane, et al., *Angew. Chem. Int. Ed.*, **2019**, *58*, 5302-5306; b) M. Hadar, et al., *Chem. Eur. J*., **2020**, *26*, 11250-11255.

P5 Novel Molecular Receptors for the Recognition, Sensing and Transport of Anions

Jolliffe K. A.[a,b,c]

[a] *School of Chemistry, The University of Sydney, NSW 2006, Australia;* [b] *Australian Research Council Centre of Excellence for Innovations in Peptide and Protein Science, The University of Sydney, NSW 2006, Australia;* [c] *The University of Sydney Nano Institute (Sydney Nano), The University of Sydney, NSW 2006, Australia.*

E-mail: kate.jolliffe@sydney.edu.au

The selective recognition of anions has numerous applications in areas as diverse as the environment and medicine. Most of these applications require anion recognition to occur in a competitive aqueous environment, but the design of receptors capable of selective binding to anions in water is difficult, predominantly as a result of the high hydration energy of anionic species.

In natural systems, highly efficient and selective anion recognition is achieved through the use of large peptides and proteins that take advantage of the numerous H-bonding interactions available from a variety of amino acid side chains with additional contributions from the amide protons in the protein backbone. Metal-ligand interactions from protein-bound metal ions to anions are also common in biological anion binding. This has inspired our research into the development of synthetic anion receptors that combine both natural and non-natural binding motifs. We present here novel anion receptors, comprising both macrocyclic and linear scaffolds displaying hydrogen bonding motifs and transition metal binding sites, that are capable of selective anion recognition, extraction or transport.

I19 Nonporous Adaptive Crystals (NACs) for Separation and Adsorption

Huang F.

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China.
E-mail: fhuang@zju.edu.cn

In this talk, I will introduce a novel kind of solid materials for adsorption and separation, nonporous adaptive crystals (NACs), which function at the supramolecular level.[1] They are nonporous in the initial crystalline state, but the intrinsic or extrinsic porosity of the crystals along with a crystal structure transformation is induced by preferable guest molecules. Unlike solvent-induced crystal polymorphism phenomena of common organic crystals that occur at the solid-liquid phase, NACs capture vaporized guests at the solid-gas phase. Upon removal of guest molecules, the crystal structure transforms back to the original nonporous structure. I will focus on the discussion of pillararene-based NACs for adsorption and separation and the crystal structure transformations from the initial nonporous crystalline state to new guest-loaded structures during the adsorption and separation processes. Compared with traditional porous materials, NACs of pillararenes have several advantages. First, their preparation is simple and cheap and they can be synthesized in large-scale to meet practical demands. Second, pillararenes have better chemical, humid and thermal stability than crystalline MOFs, COFs and POCs, which are usually constructed based on reversible chemical bonds. Third, pillararenes are soluble in many common organic solvents, which means that they can be easily processed in solution. Fourth, their regeneration is simple and they can be reused many times with no decrease in performance. It is expected that this kind of materials will not only exert significant influence on scientific research, but also show practical applications in the chemical industry.

References

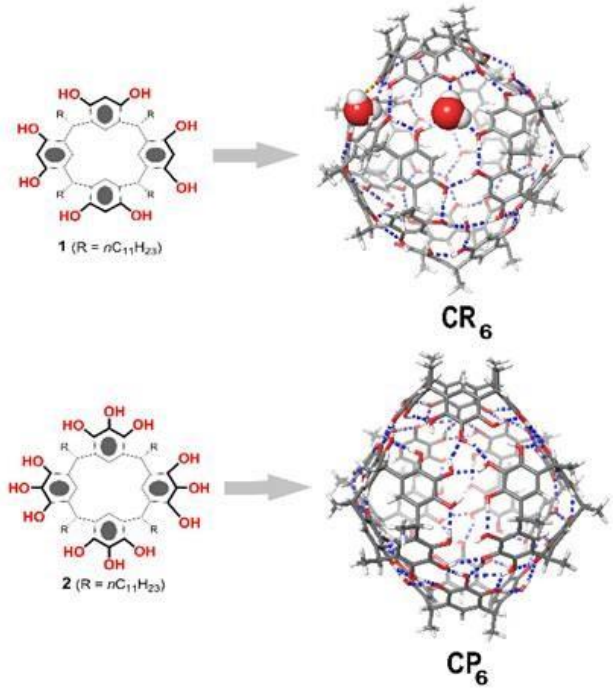
1. a) K. Jie, M. Liu, Y. Zhou, M. A. Little, S. Bonakala, S. Y. Chong, S. Y. Stephenson, L. Chen, F. Huang, A. I. Cooper, *J. Am. Chem. Soc.* **2017**, *139*, 2908; b) K. Jie, Y. Zhou, E. Li, Z. Li, R. Zhao, F. Huang, *J. Am. Chem. Soc.* **2017**, *139*, 15320; c) K. Jie, Y. Zhou, E. Li, R. Zhao, M. Liu, F. Huang, *J. Am. Chem. Soc.* **2018**, *140*, 3190. d) K. Jie, M. Liu, Y. Zhou, M. A. Little, A. Pulido, S. Y. Chong, A. Stephenson, A. R. Hughes, F. Sakakibara, T. Ogoshi, F. Blanc, G. M. Day, F. Huang, A. I. Cooper, *J. Am. Chem. Soc.* **2018**, *140*, 6921. e) K. Jie, Y. Zhou, E. Li, F. Huang, *Acc. Chem. Res.* **2018**, *51*, 2064. f) K. Jie, Y. Zhou, E. Li, R. Zhao, F. Huang, *Angew. Chem. Int. Ed.* **2018**, *57*, 12845. g) E. Li, K. Jie, Y. Zhou, R. Zhao, F. Huang, *J. Am. Chem. Soc.* **2018**, *140*, 15070. h) E. Li, K. Jie, Y. Zhou, R. Zhao, B. Zhang, Q. Wang, J. Liu, F. Huang, *ACS Appl. Mater. Interfaces* **2018**, *10*, 23147. i) E. Li, Y. Zhou, R. Zhao, K. Jie, F. Huang, *Angew. Chem. Int. Ed.* **2019**, *58*, 3981-3985. j) Y. Zhou, K. Jie, R. Zhao, F. Huang, *J. Am. Chem. Soc.* **2019**, *141*, 11847. k) Q. Li, H. Zhu, F. Huang, *J. Am. Chem. Soc.* **2019**, *141*, 13290. l) M. Wang, J. Zhou, E. Li, Y. Zhou, Q. Li, F. Huang, *J. Am. Chem. Soc.* **2019**, *141*, 17102.

I20 Catalysis Mediated by Hexameric Capsules

Neri P.

Dipartimento di Chimica e Biologia "A. Zambelli", Università di Salerno, Via Giovanni Paolo II 132, I-84084 Fisciano (Salerno), Italy.
E-mail: neri@unisa.it

In the last few years, our group has been investigating several aspects of calixarene-mediated catalysis with a particular focus on supramolecular catalysis inside the confined nanospace of the self-assembling hexameric resorcinarene or pyrogallolarene capsule.[1] In this lecture we will report on our most recent results in this field including the catalytic role of the bridged water molecules of the resorcinarene capsule **CR_6**[2] and how to make the pyrogallol[4]arene capsule **CP_6** catalytically active by exploiting a non-competitive solvent.[3]



References

1. a) C. Gaeta, C. Talotta, M. De Rosa, P. La Manna, A. Soriente, P. Neri, *Chem. Eur. J.* **2019**, *25*, 4899–4913; b) C. Gaeta, P. La Manna, M. De Rosa, A. Soriente, C. Talotta, P. Neri, *ChemCatChem.* **2020**, *13*, 1638–1658; c) C. Gaeta, C. Talotta, M. De Rosa, P. La Manna, A. Soriente, P. Neri, in *Reactivity in Confined Spaces* (Eds: R. S. Forgan, G. O. Lloyd), RSC, **2021**, Chapt. 5, pp. 133–166; d) C. Gaeta, C. Talotta, M. De Rosa, A. Soriente, A. Rescifina, P. Neri in *Supramolecular Catalysis: New Directions and Developments* (Eds: P.W.N.M. van Leeuwen, M. Raynal), WILEY-VCH, **2022**, Chapt. 23, 335–346.
2. a) P. La Manna, C. Talotta, G. Floresta, M. De Rosa, A. Soriente, A. Rescifina, C. Gaeta, P. Neri, *Angew. Chem. Int. Ed*., **2018**, *57*, 5423–5427; b) S. Gambaro, C. Talotta, P. Della Sala, A. Soriente, M. De Rosa, C. Gaeta, P. Neri, *J. Am. Chem. Soc.* **2020**, *142*, 14914–14923.
3. P. La Manna, C. Talotta, C. Gaeta, Y. Cohen, S. Slovak, A. Rescifina, P. Della Sala, M. De Rosa, A. Soriente, P. Neri, *Org. Chem. Front*. **2022**, *9*, DOI: 10.1039/d2qo00172a.

I21 Solid State Self-Assembly of Organic/Inorganic Hybrids

Smith B. D., Shaffer C. C., Liu W., Oliver A. G.

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA;
E-mail: smith.115@nd.edu

Self-assembly of solid state organic/inorganic hybrids is a promising way to rapidly prepare advanced materials with novel properties. The development of biomimetic nanocomposites is especially interesting since it provides insight into the natural mechanisms for creation and remodeling of biominerals. The lecture will summarize two separate supramolecular projects that use organic and inorganic building blocks to create solid-state hybrid materials, with an emphasis on the supramolecular rules that govern the self-assembly processes.

The first project uses a series of organic receptor molecules to co-precipitate square planar gold(III) coordination complexes and form co-crystals. The work has potential utility in a wide range of fields that involve precious metals, including mining, recycling, and nanoscience. X-ray diffraction analysis reveals the presence of three dominant supramolecular interactions; (a) hydrogen bonding between amide NH residues and the AuX_4^- anion, (b) electrostatic stacking of the Au center against aromatic π-electrons, (c) very short hydrogen bonds within a proton-bridged-carbonyls motif (Figure 1, left). One set of studies found that a sterically-geared receptor was consistently trapped in a high energy molecular conformation which increased the number of favorable intermolecular interactions in the lattice. The results support two generalizable rules that will improve co-crystal structure prediction.

The second project reports an unprecedented new procedure for clean conversion of mesoporous silica nanoparticles into hollow structures in one step under mild conditions (Figure 1, right). Moreover, the organic molecules are incorporated within the shell of the hollow silica nanoparticles. The structural scope of the organic molecule includes FDA-approved drugs and fluorescent dyes, with the promise of new therapeutic and imaging applications.

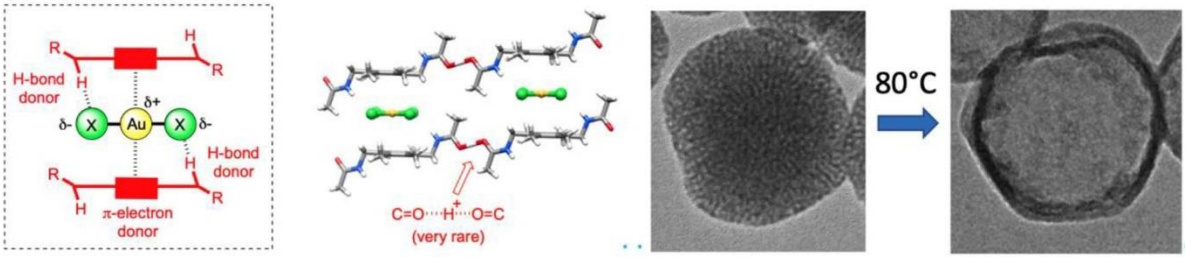


Figure 1. (*left*) Co-crystal engineering of gold composites. (*right*) One step organic templated conversion of mesoporous silica nanoparticles into hollow silica nanoparticles (100 nm diameter).

References

1. a) C. C. Shaffer, B. D. Smith, *Org. Chem. Front.*, **2021**, *8*, 1294-1301; b) C. C. Shaffer, W. Liu, A. G. Oliver, B. D. Smith, *Chem Eur. J.*, **2021**, *27*, 751-757. c) W. Liu, A. G. Oliver, B. D. Smith, *J. Am. Chem. Soc.* **2018**, *140*, 6810-6813.

C16 Expanding the Toolbox of Dynamic DNA Chemistry with Macrocyclic Hosts

Jayawickramarajah J.

Department of Chemistry, Tulane University, 2015 Percival Stern Hall, New Orleans, Louisiana, USA.
E-mail: jananj@tulane.edu

The development of information processing molecular- and nano-machines and their higher-order interaction networks is a multi-disciplinary research area that has seen major growth. In order to achieve practical applications, such machines need to be coupled to the outside world. Hence, it is salient to develop systems that function effectively in water/biological media. In this talk, we describe how supramolecular chemistry, and especially macrocyclic chemistry, can be harnessed in combination with DNA to generate dynamic systems with potential therapeutic and diagnostic applications. We will begin by discussing the synthesis and development of macrocycle-DNA conjugates (cyclodextrin-DNA, cucurbit[n]uril(CB)-DNA, and porphyrin-DNA) that have enhanced fluorescence or are activated via specific biological inputs, including nucleic acid sequences and small biomolecules, such as adenosine triphosphate.[1-3] In the second half of the talk, we introduce a novel concept wherein DNA strand displacement is controlled by CB[7]-based host-guest chemistry. In an effort to expand the toolbox of dynamic DNA chemistry, we show how such a synthetic strand displacement process can be (a) finely controlled and (b) integrated into functional devices that control protein activity and layered reactions that detect specific microRNA.

References

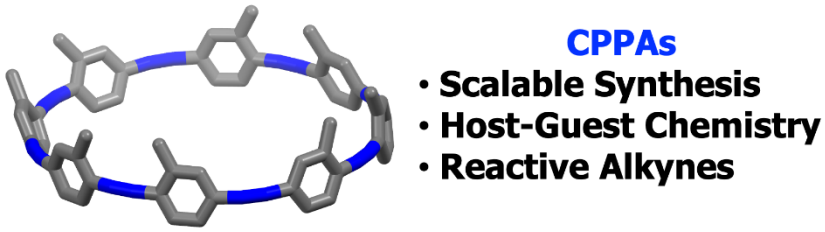
1. X. Zhou, X. Su, P. Pathak, R. Vik, B. Vinciguerra, L. Isaacs, J. Jayawickramarajah, *J. Am. Chem. Soc.* **2017**, *139*, 13916-13921.
2. P. Pathak, W. Yao, K. D. Hook, R. Vik, F. R. Winnerdy, J. Q. Brown, B. C. Gibb, Z. F. Pursell, A. T. Phan, J. Jayawickramarajah, *J. Am. Chem. Soc.* **2019**, *141*, 12582-12591.
3. S. Pandey, D. Kankanamalage, X. Zhou, C. Hu, L. Isaacs, J. Jayawickramarajah, H. Mao, *J. Am. Chem. Soc.* **2019**. *141*, 18395-18389.

C17 Scalable Synthesis and Applications of Cycloparaphenyleneacetylene Carbon Nanohoops

Lee S., Zhou X., Herman R. J., LaFleur L.

Department of Chemistry, Louisiana State University.
E-mail: seminlee@lsu.edu

Cycloparaphenyleneacetylenes (CPPA) by Kawase and Oda in 1996[1] were one of the earliest carbon nanohoops that were synthesized. Due to the curved phenylenes and strained alkynes, CPPAs have unique photophysical and supramolecular properties. Here, we present a high-yielding and scalable preparation of CPPA derivatives.[2-4] Alkyne metathesis is used as a dynamic covalent method to achieve high-yielding macrocyclization. We also introduce host-guest complexes that take advantage of the large central binding site of CPPAs. The strained alkyne groups serve as reactive sites for various strain-promoted reaction.



References

1. T. Kawase, H. R. Darabi, M. Oda, *Angew. Chem. Int. Ed.* **1996**, *35*, 2664.
2. S. Lee, E. Chenard, D. L. Gray, J. S. Moore, *J. Am. Chem. Soc.* **2016**, *138*, 13814.
3. X. Zhou, R. R. Thompson, F. R. Fronczek, S. Lee, *Org. Lett.* **2019**, *21*, 4680.
4. X. Zhou, H. Kwon, R. R. Thompson, R. J. Herman, F. R. Fronczek, C. J. Bruns, S. Lee, *Chem. Commun.* **2021**, 57, 10887.

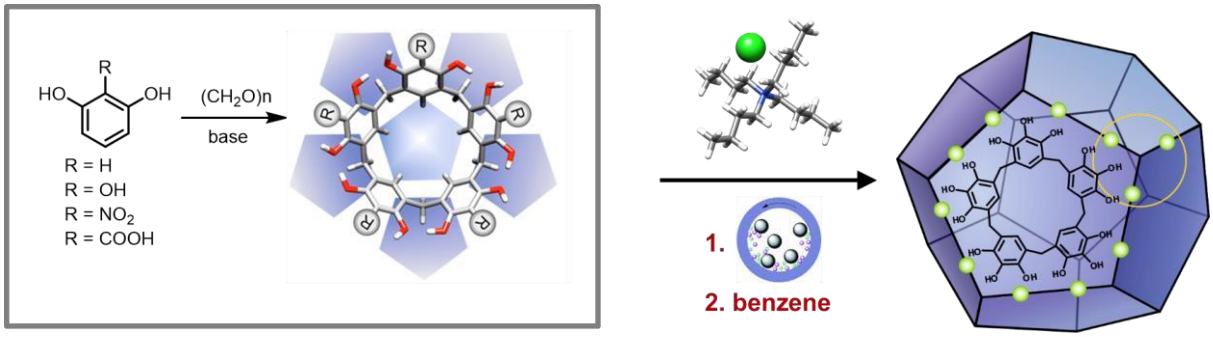
I22 Mechanochemistry of Molecular Containers

Szumna A.

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

E-mail: agnieszka.szumna@icho.edu.pl

In Nature, self-assembly typically occurs under far-from-equilibrium and specific local conditions (e.g. locally low dielectric or locally high concentration). Thus, local environment promotes formation of species that might not survive in bulk-solvent environment. In supramolecular chemistry, the self-assembly processes are typically studied under thermodynamic equilibrium conditions, which implies that some structures, functions and complexity of matter may never be achieved. We suggest that mechanochemistry is a method that induces self-assembly and complexation under specific local environment with high local concentration of components, absence of competitive interactions with solvent, and presence of friction forces. Mechanochemistry, besides creation of specific local conditions, offers numerous additional advantages: it is eco-friendly (no waste solvents), cheap and easy to execute at various scales (commercial mills of various capacities are available). Despite that, it is rarely used to induce self-assembly and encapsulation and the mechanisms remain only vaguely known. We show that application of mechanochemistry enables formation self-assembled species that are hard or even impossible to obtain under the classic bulk solution conditions. Particularly, anion-sealed molecular capsules based on polyphenolic macrocycles and various covalent complexes. can be formed.



References

1. M. Chwastek, P. Cmoch, A. Szumna, *J. Am. Chem. Soc.* **2022**, DOI:10.1021/jacs.1c11793.
2. M. Chwastek, P. Cmoch, A. Szumna, *Angew. Chem. Int. Ed.* **2021**, *60*, 4540-4544.
3. M. Chwastek, A. Szumna, *Org. Lett.* **2020**, *22*, 6838−6841.

P6 Measuring anion binding at biomembrane interfaces

Gale P. A.,[a] Wu X.,[a] Wang P.,[a] Lewis W.,[a] and Jiang Y.-B.[b]

[a]School of Chemistry, The University of Sydney NSW 2006, Australia; [b]Department of Chemistry, Xiamen University 361005, China.

E-mail: philip.gale@sydney.edu.au

Molecular interactions at biomembrane interfaces[1] are ubiquitous in many biological processes and underpin several mechanisms of drug actions.[2] Despite the important biological regulatory roles of transmembrane anion transport, fundamental knowledge of anion binding to natural or synthetic molecules within lipid bilayers is lacking[3] in contrast to the better-understood solution-phase studies.[4] In this presentation we show how to bridge this knowledge gap by making anion binding measurable within lipid bilayers. This was achieved using a macrocycle that has a record aqueous SO_4^{2-} affinity among neutral receptors which increases fluorescence on SO_4^{2-} binding. We show that in lipid bilayers the determinants of anion binding are extraordinarily different from those expected that govern anion binding in solution. Charge-dense anions $H_2PO_4^-$ and Cl^- that prevail in DMSO fail to bind to the macrocycle in lipids. In stark contrast, ClO_4^- and I^- that hardly bind in DMSO show surprisingly significant affinities for the macrocycle in lipids. We have revealed a lipid bilayer anion binding principle that depends on anion polarisability and bilayer penetration depth of complexes leading to unexpected advantages of charge-diffuse anions. These insights enhance our understanding of how biological systems select anions and guide the design of functional molecular systems operating at biomembrane interfaces.[5]

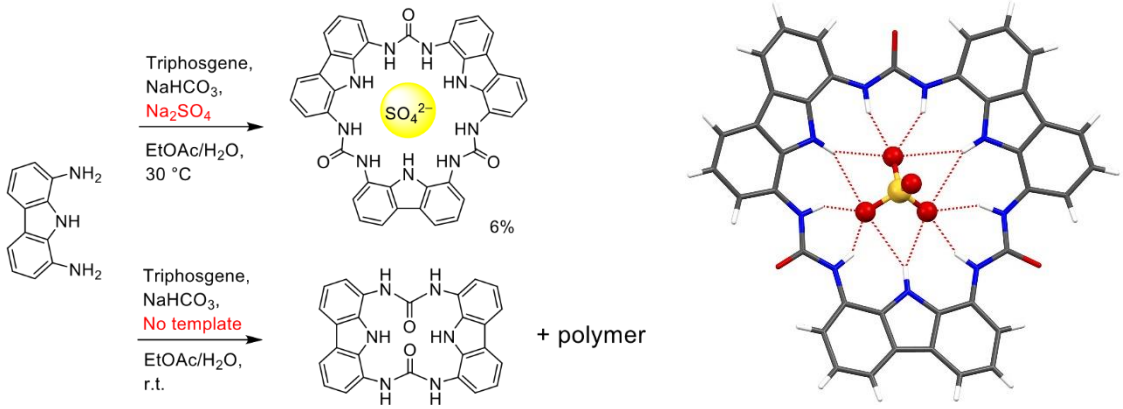


Figure 1. Synthesis and crystal structure of the sulfate complex of the carbazole-urea macrocycle used in these studies.

References

1. G. Gonella et al. *Nat Rev. Chem.* **2021**, *5*, 466-485.
2. a) K.A. Muraglia et al. *Nature* **2019**, *567*, 405-408; b) V. Kaushik, J.S. Yakisich, A. Kumar, N. Azad and A.K.V. Iyer, *Cancers*, **2018**, *10*, 360; c) N. Busschaert et al., *Nature Chem*. **2017**, *9*, 667-675; d) H. Li et al. *Nature Chem*. **2016**, *8*, 24-32.
3. P.S. Cremer, A.H. Flood, B.C. Gibb,and D.L. Mobley, *Nature Chem.* **2017**, *10*, 8.
4. a) T. Fiala, K. Sleziakova, K. Marsalek, K. Salvadori and V. Sindelar, *J. Org. Chem.* **2018**, *83*, 1903-1912; b) Y. Liu, A. Sengupta, K. Raghavachari and A.H. Flood, *Chem*, **2017**, *3*, 411-427; c) F. Sommer, Y. Marcus and S. Kubik, *ACS Omega*, **2017**, *2*, 3669-3680; d) N. Busschaert, C. Caltagirone, W. Van Rossom and P.A. Gale, *Chem. Rev.* **2015**, *115*, 8038-8155.
5. X. Wu, P. Wang, W. Lewis, Y.-B. Jiang and P.A. Gale, *ChemRxiv,* **2022**, Preprint DOI: 10.26434/chemrxiv-2021-6w803-v3.

POSTER ABSTRACTS

P1 Host Complexation with Modified Cytidines: Towards Supramolecular Prodrug Systems for Nucleoside Analogs

Beltrami N., Xiao M., Suating, P., Jayawickramarajah J.

Department of Chemistry, Tulane University, New Orleans, LA 70118, U.S.A.
E-mail: nbeltram@tulane.edu

Nucleoside analogs are a class of therapeutic agents with potent anticancer and antiviral properties. One significant limitation, however, is their swift metabolism and short plasma half-life [1]. Current prodrugs such as Capecitabine help limit plasma degradation and facilitate cellular uptake. These prodrugs are enzymatically cleaved into their parent drugs within the cell; carbamate functionalization is often preferred to control their hydrolytic stability and dynamics [2]. We envisioned that bioconversion may be further fine-tuned by inducing host-guest complexation near the carbamate, preventing substrate-active site binding.
Through a 5-step synthesis, we prepared a carbamate-based nucleoside analog through carbamoylation of Cytidine's exocyclic amine; a key step included the introduction of a terminal trimethylammonium moiety to enable better host complexation. The binding interactions of the modified cytidine with various cucurbiturils were evaluated and the effect of host-guest interactions on esterase activity was investigated.

Supramolecular chemistry, through non-covalent bonding and stimuli/environment-controlled interactions, may provide a fresh perspective in the realm of drug delivery systems. By designing and investigating a cucurbituril based host-guest system with potential nucleoside analog based chemotherapeutics, this project aims to set a foundation for future research regarding the supramolecular manipulation of the pharmacokinetics, pharmacodynamics, and potential therapeutic effects of anti-metabolites.

References

1. P. Couvreur, et al. *Nano Lett.* **2006**, *6*, 2544-2548.
2. A. K. Ghosh, M. Brindisi, *J. Med. Chem.* **2015**, *58*, 2895-2940.

P2 Ionic Resorcinarenes Target Pyrophosphate and αA66-80 Peptide Related to Cataracts

Beyeh N. K.

Department of Chemistry, Oakland University, 146 Library Drive, Rochester, MI 48309-4479, USA
E-mail: beyeh@oakland.edu

Cavity-containing macrocyclic compounds can be modified with specific functional groups and used as a target for biological materials.[1] Though it is a significant challenge to develop high-affinity receptors for anions in biologically relevant solvents, designing synthetic macrocycles that can target small bioanalytes, peptides or proteins offer a suitable avenue for applications in hybrid materials, diagnostics, and aggregation inhibitors.[2] In this talk, I will present results from two such projects:
1) Pyrophosphate (PPi) and adenosine triphosphate (ATP) are key intermediates for energy transduction and are common to several essential metabolic processes. Several diseases are strongly associated with elevated PPi levels, including cancer, arthritis, crystal deposition disease, and Paget's disease. Significant recent research effort has been focused on developing more potent PPi sensors for the early diagnosis of these conditions. We use cationic resorcinarenes and in some cases, integrated with a fluorescent tag as simple read-out high-affinity sensors for pyrophosphate.[3]
2) The αA66-80 peptide fragment of αA-crystallin, among others, was observed at a high level in cataracts eye lenses. The αA-crystallin, a heat-shock protein, maintains the solubility and stability of lens proteins and lens clarity by preventing protein aggregation, which may lead to lens clouding and eventually cataracts. We use three different ionic resorcinarene macrocycles to study how they affect αA66-80 peptide aggregation and inhibition (Figure 1).[4]

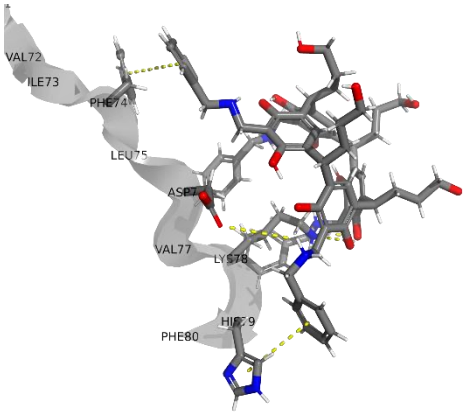


Figure 1. A resorcinarene αA66-80 peptide complex

References

1. T. Douglas, M. Young, *Nature* **1998**, *393*, 152–155.
2. A. E. Hargrove, S. Nieto, T. Zhang, J. L. Sessler, E. V. Anslyn, *Chem. Rev.* **2011**, *111*, 6603–6782.
3. N. K. Beyeh, I. Díez, S. M. Taimoory, D. Meister, A. Feig, J. F. Trant, R. H. A. Ras, K. Rissanen, *Chem. Sci.* **2018**, *9*, 1358-1367; b) K. Twum, S. I. Sadraei, J. Feder, S. M. Taimoory, K. Rissanen, J. F. Trant, N. K. Beyeh, *Org. Chem. Front.* **2022,** *9*, 1267-1275.
4. K. Twum, A. Bhattacharjee, E. T. Laryea, J. Esposto, G. Omolloh, S. Mortensen,M. Jaradi, N. L. Stock, N. Schileru, B. Elias, E. Pszenica, T. M. McCormick, S. Martic, N. K. Beyeh, *RSC Med. Chem.* **2021**, *12*, 2022-2030.

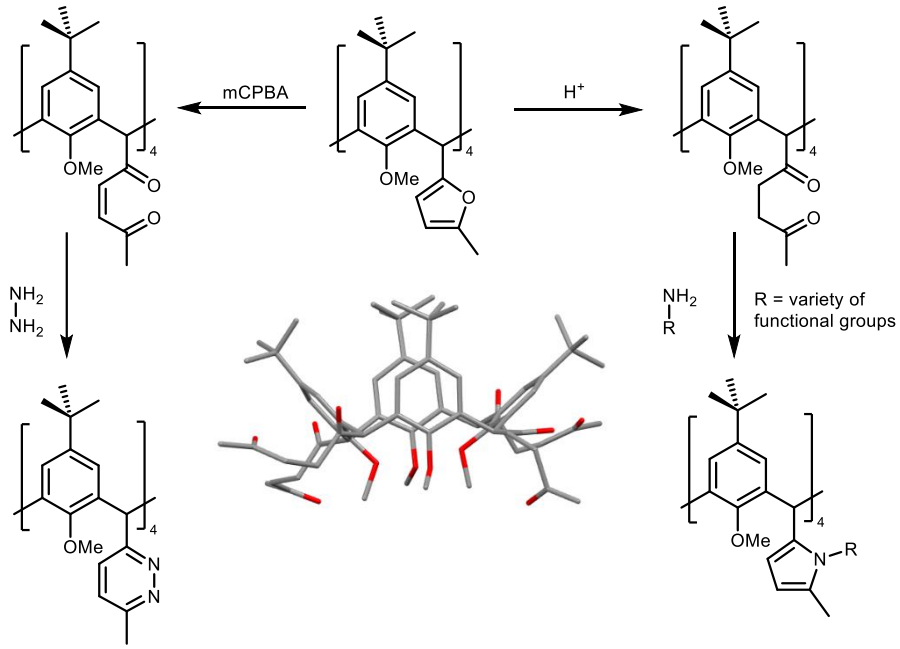
P3 Facile Synthetic Routes to Bridge-Functionalised Calix[4]arenes

Campbell C.L.,[a] Fong A.,[a] Huynh S.,[a] McCormick McPherson L.J.,[b] Teat S.J.,[b] Bebbington M.W.P.,[a,c] Dalgarno S.J.[a]

[a] Institute of Chemical Sciences, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS, UK; [b] Station 11.3.1, Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, USA; [c] Department of Chemistry and Biochemistry, Montclair State University, 1 Normal Ave., Montclair, NJ 07043, USA.

E-mail: CLC1@hw.ac.uk

The development of facile synthetic routes to bridge functionalized calix[4]arenes. This work describes the ring-opening of furans which are monosubstituted at every equatorial methylene bridge position of a calix[4]arene. This in turn provides access to a range of new molecules (in good yield) that have widespread potential impact in supramolecular chemistry amongst other areas.



References

1. a) A. Fong, L. McCormick, S. J. Teat, E. K. Brechin and S. J. Dalgarno, *Supramol. Chem.*, **2018**, 30, 504–509. b) A. Fong, C. L. Campbell, S. Huynh, L. J. McCormick McPherson, S. J. Teat, M. W. P. Bebbington and S. J. Dalgarno, *Chem. Commun.*, **2022**, 58, 3302–3305. c) I. Columbus and S. E. Biali, *Org. Lett.*, **2007**, 9, 2927–2929.

P4 Shaking Ureido and Carboxylic Hands – Calixarenes Uniting

Cvetnić M., Bregović N., Cindro N., Tomišić V.

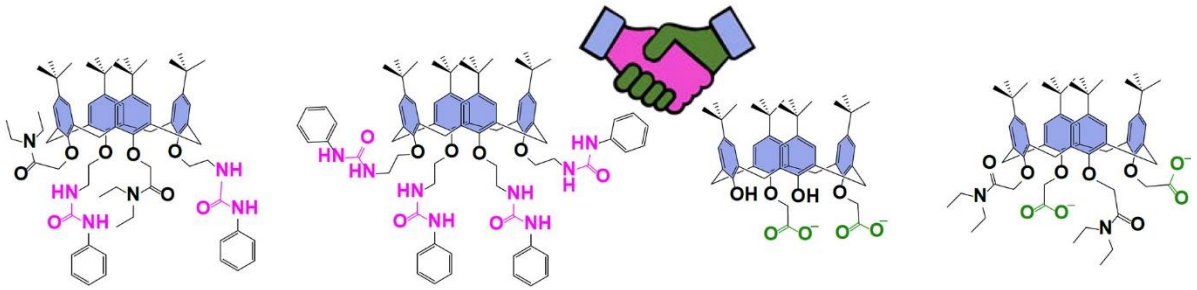
Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia

E-mail: marija.cvetnic@chem.pmf.hr

Covering many application areas such as sensing, extraction, self-assembly, transport, and catalysis, investigations in anion receptor chemistry are very important.[1] Calixarenes functionalized with (thio)urea as hydrogen-bond donating groups can serve as classical anion receptors, but also as building blocks for molecular containers[2] and, more recently, as selective binders and transporters of different biochemically relevant species.[3,4]

Recently, we have prepared two *p*-tert-butylcalix[4]arene derivatives bearing urea moieties (**1**, **2**), determined their pK_a values and investigated their complexation with several anions (Cl^-, HSO_4^-, $H_2PO_4^-$, benzoate, and hydrogen pyrophosphate) in acetonitrile. Macrocycle **2** is better anion binder than **1** due to more urea groups present in its structure and lower pK_a values. Complexes of 1:2 and 2:1 stoichiometry (as receptor:anion) were observed with $H_2PO_4^-$ and hydrogen pyrophosphate, respectively. Compound **1** was also designed as ion-pair receptor, so cooperative effect of binding of Na^+ on the complexation of several anions with **1** was thermodynamically quantified.

Herein, the thermodynamics of acetate binding with **1** and **2** was characterized using ^{1}H NMR, UV-Vis, and ITC. Relatively high values of stability constants of the corresponding complexes (log $\beta_{11} > 4$) were determined and the formation of $\mathbf{1}_2AcO^-$ complex was detected. These results motivated the research of possible capsule formation between ureido-calix[4]arene derivatives and diacetatocalix[4]arenes (**3**, **4**) via hydrogen bonding between the urea and carboxylate moieties. Indeed, the uniting of the two types of calixarenes into very stable (especially for **2**) complexes was observed using the above methods as well as DOSY and conductometry. Tertiary amide groups in carboxylic calix[4]arene **4** lowered the affinity for its *handshake* with calixarene **2** in comparison to **1**.



1 **2** **3** **4**

Figure 1. Structures of the investigated calixarene derivatives.

References

1. L.K. Macreadie, A.M. Gilchrist, D.A. McNaughton, W.G. Ryder, M. Fares, P.A. Gale, *Chem* **2022**, *8*, 46–118.
2. G. Aragay, P. Ballester, in *Calixarenes and Beyond* (Eds: P. Neri et al.), Springer, **2016**, pp. 843–878.
3. S. Moerkerke, J. Wouters, and I. Jabin, *J. Org. Chem.* **2015**, *80 (17)*, 8720–8726.
4. G. Grauwels, H. Valkenier, A. P. Davis, I. Jabin, and K. Bartik, *Angew. Chem.* **2019**, *58 (21)*, 6921–6925.

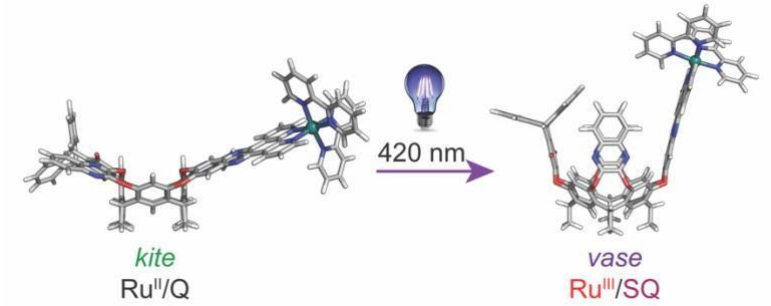
P5 Stimuli-Responsive Resorcin[4]arene Cavitands: Toward Visible Light-Activated Molecular Grippers

García-López V,[a,b] Zalibera M.,[c] Trapp N.,[b] Wenger O. S.,[d] Diederich F.[b]

[a] Department of Chemistry, Louisiana State University, 349 Chemistry and Materials Building, Baton Rouge LA 70806; [b] Laboratory of Organic Chemistry, ETH Zurich, HCI Vladimir-Prelog-Weg 3, Zurich, Switzerland 8093; [c] Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology, Radlinského 9, Bratislava, Slovakia 81237; [d] Department of Chemistry, University of Basel, St. Johanns-Ring 19, Basel Switzerland 4056.

E-mail: vglopez@lsu.edu

We synthesized and investigated a series of multi-stimuli responsive resorcin[4]arene cavitands equipped with quinone (**Q**) and $[Ru(bpy)_2dppz]^{2+}$ photosensitizing walls in different configurations. The cavitands exhibit a large conformational switching from an expanded *kite* to a contracted *vase* with a deep cavity upon visible light irradiation, chemical and electrochemical redox activation, and hostguest interactions in the ground state. Upon visible light irradiation, electron transfer from the $[Ru(bpy)_2dppz]^{2+}$ to the **Q** generates the semiquinone (**SQ**) radical anion, triggering the large conformational switching. Depending on the molecular design, the **SQ** radical can live for several minutes (~10 min), and the *vase* can be generated in a secondary process without the addition of a sacrificial electron donor. These systems overcome three limitations of previous designs: the need for a sacrificial donor to accumulate the short-living **SQ** (~ s), and the inability to form a *vase*, and capture guest molecules. This study provides insights into the development of stimuli-responsive molecular grippers for transmembrane delivery, nanofabrication, sensor technologies, or switchable units in materials that require significant conformational changes.



References

1. a) V. García-López, M. Zalibera, N. Trapp, M. Kuss-Petermann, O. Wenger, F. Diederich, *Chem. Eur. J.* **2020**, *26*, 11451–11461; b) V. García-López, J. Milić, M. Zalibera, D. Neshchadin, M. Kuss-Petermann, L. Ruhlmann, J. Nomrowski, N. Trapp, C. Boudon, G. Gescheidt, O. S. Wenger, F. Diederich, *Tetrahedron* **2018**, *74*, 5615–5626.

P6 Amphiphilic Cavitands as Antibacterial Agents

Hebert A. J., Gibb C.L.D., Busschaert N., Gibb B.C.

Department of Chemistry, Tulane University, New Orleans, Louisiana, United States
E-mail: ahebert12@tulane.edu

Our group specializes in the synthesis of resorcinarene-based cavitands, most notably the deep-cavity cavitand octa acid.[1,2] Through modification of the upper rim and low pendent groups ("feet") of the resorcinarene scaffold, their physicochemical properties can be tailored to meet specific needs. Inspired by several studies within the literature demonstrating strong antimicrobial properties of charged macrocyclic hosts,[3-5] we have synthesized a variety of cavitands whereby the feet and the rim are respectively substituted by charged groups and long alkyne chains. These have been tested against common strains of bacteria for their antimicrobial activity. Our results show that an amphiphilic tetra-hexyne-tetra-trimethylammonium chloride cavitand (Figure 1, n = 1) exhibits an exceptionally low minimum inhibitory concentration value. Building on this, we will report our latest findings concerning the synthesis and anti-microbial properties of a range of amphiphilic cavitands, particularly those possessing different lengths of alkyne chains and different positive charged groups at the feet.

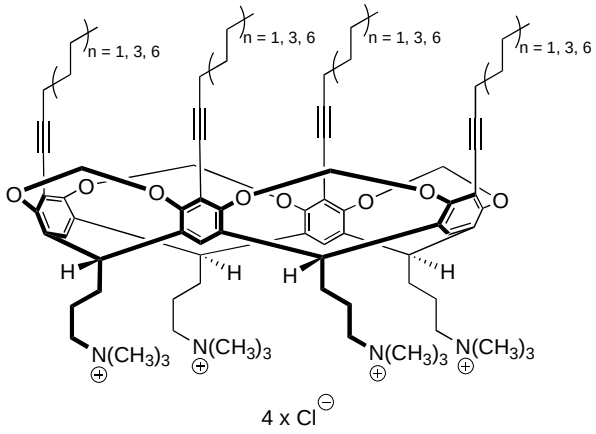


Figure 1. Chemical structure of tetra-alkyne-tetra-trimethylammonium chloride cavitands.

References

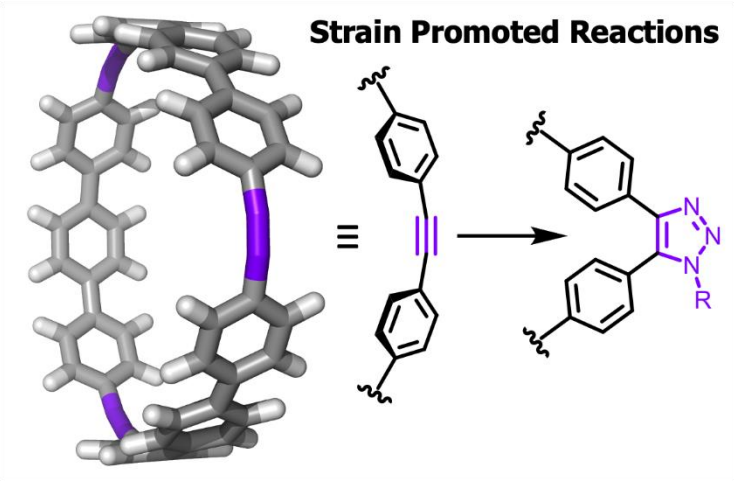
1. S. Liu, S.E Whisenhunt-loup, C.L.D Gibb, & B.C Gibb, *Supramol Chem*. **2011,** *24*, 480-5.
2. C.L.D. Gibb and B.C. Gibb, *J Am Chem Soc*. **2004**, *126*, 11408-9.
3. E.S. Williams, H. Gneid, S.R. Marshall, M.J. Gonzalez, J.A. Mandelbaum, & N. Busschaert, *Org Biomol Chem.* **2021**.
4. S.R. Herschede, H. Gneid, T. Dent, E.B. Jaeger, L.B. Lawson, & N. Busschaert, *Org Biomol Chem*. **2021**, *19*, 3838-43.
5. D.N. Shurpik, P.L. Padnya, I.I. Stoikov, & P.J. Cragg, *Molecules*. **2020**, *25*, 5145.

P7 Strain-Promoted Reactions on Cycloparaphenyleneacetylene Derivatives

Herman R., Zhou X., LaFleur L., Lee S.

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803
E-mail: rherma6@lsu.edu

Recent advances in alkyne metathesis have allowed for facile synthesis of cycloparaphenyleneacetylene (CPPA) carbon nanohoops.[1] Most notably, we are now able to prepare [8]CPPA in gram-scale quantities.[2] CPPAs have strained alkynes within their backbone that undergo various strain-promoted reactions including azide-alkyne [3+2] cycloadditions.[1,3] Herein, the reactivity of a [8]CPPA derivative is explored via [3+2] cycloaddition with various azido compounds. The kinetics of these reactions are compared to Sondheimer diyne,[4] an archetypal cyclooctadiyne with two strained alkynes.



References

1. S. Lee, J. Moore, *JACS* **2016**, *138*, 13814-13817
2. X. Zhou, R. Herman, S. Lee, *Chem Commun.* **2021**, *57*, 10887-10890
3. T. Schaub, R. Jasti, *ACIE* **2018**, *57*, 16348-16353
4. I. Kii, T. Hosoya, *Org. Biomol. Chem.* **2010**, *8*, 4051-4055

P8 Towards Developing Organo-Catalysts in Aqueous Media

Ismaiel Y.A., and Bruce C. Gibb

Tulane University, New Orleans, Louisiana, United States
E-mail: yismaiel@tulane.edu

Toward efficient catalysis in water, the deep-cavity cavitand octa-acid 1 has been utilized as a yocto-liter (10^{-24} L) reaction vessel through self-assembly via the hydrophobic effect.[1,2] Cyclization reactions inside 1_2 have been previously reported, but catalysis was not usually observed because of product inhibition.[3,4] One of our goals is to identify the key factors that overcome product inhibition and engender catalysis within such structurally defined hosts. Towards this, we will report on how leaving group size (and hence the change in volume between starting material and product) can be used to induce catalytic turnover in the synthesis of difficult to make medium sized rings.[5] We will also report on progress in our studies of cyclization processes that ostensibly go through S_N1 mechanisms, and how the nature of the charge of the capsule affects this.

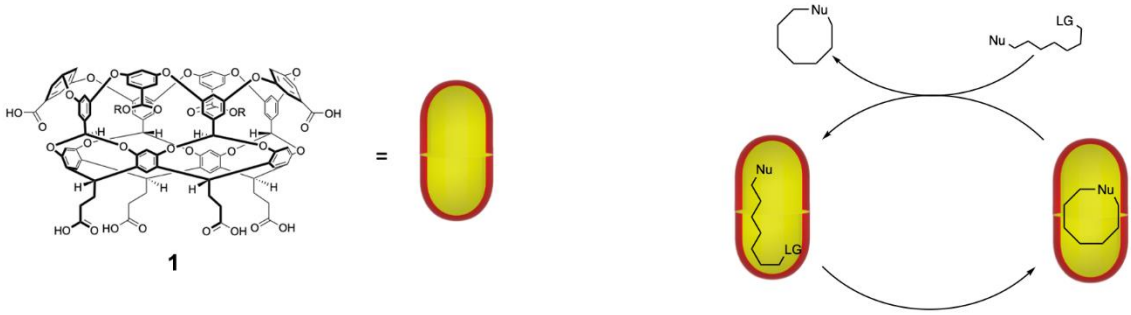


Figure 1. Octa acid **1** via encapsulation inducing catalysis and the formation of medium sized rings.

References

1. C. L. D. Gibb, B. C. Gibb, *J. Am. Chem. Soc* **2004,** *126* (37), 11408-11409.
2. M. B. Hillyer, C. L. D. Gibb, P. Sokkalingam, J. H. Jordan, S. E. Ioup, B. C. Gibb, *Org. Lett.* **2016,** *18* (16), 4048-4051.
3. K. Wang, X. Cai, W. Yao, D. Tang, R. Kataria, H. S. Ashbaugh, L. D. Byers, B. C. Gibb, *J. Am. Chem. Soc.* **2019**, *141* (16), 6740-6747.
4. W. Yao, K. Wang, Y. A. Ismaiel, R. Wang, X. Cai, M. Teeler, B. C. Gibb, *J. Phys. Chem.* **2021,** *125* (32), 9333-9340.
5. C. Galli, L. Mandolini, *Eur. J. Org. Chem*. **2000,** *2000* (18), 3117-3125.

P9 Fluorescent ESIPT Macrocycles: Tetrakis(2-benzimidazole)resorcin[4]arenes

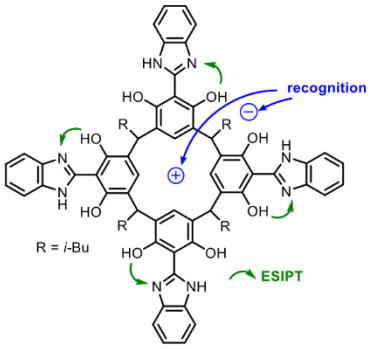
Jurek P., Szumna A.

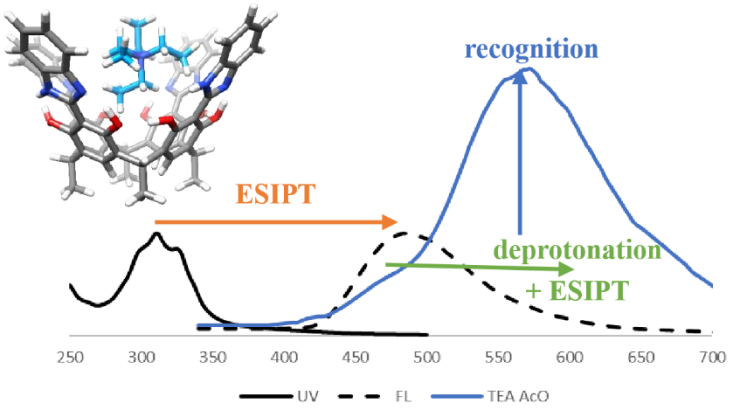
Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

E-mail: pjurek@icho.edu.pl

Fluorescence, due to great sensitivity, easy operation, biocompatibility, and high safety is the most widely used optical signal for chemical sensing and biological imaging. Calixarenes and related macrocycles are privileged scaffolds for selective binding because they provide a restrictive spatial environment (cavity). To obtain fluorescent probes based on calixarenes, recognition units are typically appended with fluorescent units at the peripheries.[1, 2]

Here we present tetrakis(2-benzimidazole)resorcin[4]arenes – the core-fluorescent macrocyclic compounds containing cavities capable of complexation of guest molecules. Obtained compounds exhibit ESIPT owing to the presence of intramolecular hydrogen that enables excited-state enol-keto tautomerization These macrocyclic compounds generate a fluorescent response of the "turn-on" type and a large Stokes-shift by the combined mechanism of ESIPT and recognition-induced emission enhancement (RIEE). We demonstrate that tetrakis(2-benzimidazole)resorcin[4]arenes can be used as quantitative sensors for acetylcholine – an important analytical target being a small molecule neurotransmitter is involved in many physiological processes (regulation of muscular contraction in the motor system, ganglionic transmission in the autonomic nervous system, and transmission at the effector organs of the parasympathetic branch of the autonomic nervous system).[3]





References

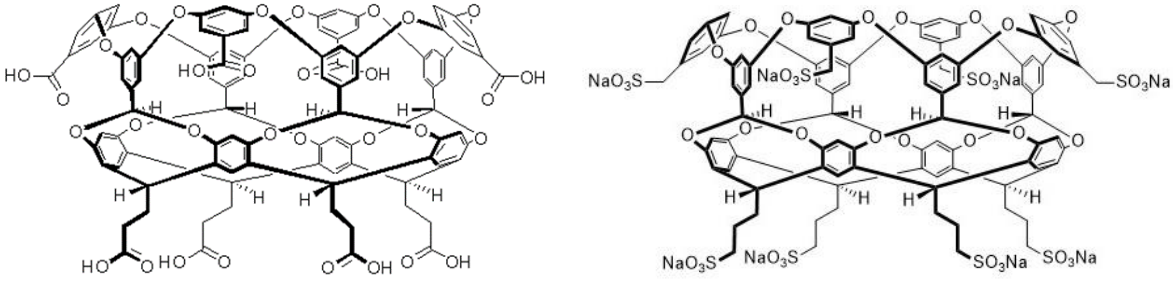
1. R. Kumar, A. Sharma, H. Singh, P. Suating, H. Seok Kim, K. Sunwoo, I. Shim, B. C. Gibb, J. Seung Kim, *Chem. Rev.* **2019**, *119*, 9657−9721;
2. A. Szafraniec, W. Iwanek, *Int. J. Mol. Sci.* **2020**, *21*, 6160.
3. T. H. Tsai, *J. Chromatography B* **2000**, *747*, 111-122.

P10 Toward the Synthesis of Negatively Charged Cavitands

Kim J.S, and Gibb B.C.

Tulane University, New Orleans, Louisiana, United States.
E-mail: skim27@tulane.edu

Cavitands are "bowl-shaped" macrocycles that are derived from the bridging of the phenolic oxygens of resorcinarenes. Variations of cavitands are achieved by modifying the nature of the bridges and the functionality on the lower rim. The bridge themselves are used to alter the width and depth of the cavitand, hence control guest encapsulation. A benzal-bridged deep-cavity cavitand that has been the key component of the group is octa-acid (Figure **1a**). [a] This host has eight carboxylic acid groups, soluble in neutral or basic conditions, and can form 1:1, 2:1, or 2:2 host-guest complexes. [b,c,d] To expand the ability of these hosts to act as yocto-liter reaction vessels [e,f], we are targeting cavitands that are negatively charged at low pH; specifically, examples with phosphonate or sulfonate water-solubilizing groups (e.g., Figure **1b**). Progress towards these hosts, as well as initial binding studies, will be described.



(**a**) (**b**)

Figure 1. Octa Acid (**a**) and octa sulfonate target (**b**)

References

1. S. Liu, S.E Whisenhunt-Ioup, C.L.D Gibb, B.C Gibb, *Supramol Chem*. **2011,** *24*, 480-5.
2. S. Liu, H. Gan, A.T. Hermann, S.W. Rick, B.C. Gibb, *Nat Chem*. **2010**, *2(10),* 847-52.
3. S. Liu, D.H. Russell, N.F. Zinnel, B.C Gibb. *J Am Chem Soc.* **2013**, 135(11), 4314-24.
4. P. Suating, T.T. Nguyen, N.E Ernst, Y. Wang, J.H. Jordan, C.L.D. Gibb, H.S. Ashbaugh, B.C. Gibb. *Chemical Science*. **2020**, *11(14),* 3656-63.
5. W. Yao, K. Wang, Y.A Ismaiel, R. Wang, X. Cai, M. Teeler, B.C Gibb. *J Phys Chem B*. **2021**, *125(32),* 9333-40.
6. K. Wang, X. Cai, W. Yao, D. Tang, R. Kataria, H.S. Ashbaugh, L.D. Byers, B.C Gibb. *J Am Chem Soc*. **2019**, *141*, 6740–7.

P11 Fingerprinting Structurally Similar Compounds using Naturally Fluorescent Acyclic-Cucurbit[n]urils and Machine Learning

King D., Murkli S., Isaacs, L.

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, United States.
E-mail: daking11@umd.edu

Acyclic-cucurbit[n]urils (aCB[n]), comprised of a glycoluril backbone capped by aromatic walls at each end, are more flexible, soluble, and functionalizable than macrocyclic CB[n] containers, while retaining the high binding affinities of the latter. Choosing intrinsically fluorescent walls allows for the synthesis of naturally fluorescent aCB[n] (NFaC) containers. The fluorescence of these containers changes in unique ways, and is a direct result of guest encapsulation. While CB[n] have been utilized in indirect assays, like indicator displacement assays (IDA),[1] NFaC offer a number of advantages because the change in the fluorescence spectra is a direct result of the host-guest binding interaction. By relying on an external fluorophore for signal, IDA does not convey any information about the size, and electronic properties of the guest which, in contrast, NFaC are able to retain.
Changes in the fluorescence spectrum of NFaC induced by guest binding can be analyzed using machine learning (ML) algorithms for pattern recognition to identify details about analyte structure.[2] Here we show that a combination of well curated fluorescence data and ML algorithms like linear discriminant analysis (LDA) can be used to differentiate 23 structurally similar guests with 91% accuracy.[3] Interestingly, it is also able to group the guests according to the substitution of the ammonium nitrogen and the quenching/enhancing nature of each analyte. By utilizing two NFaC, **M3** and **Z1,** the applicability of this technique is enhanced and allows identification and quantification of drugs of abuse like cocaine, and fentanyl at ng/mL concentrations in complex mixtures.

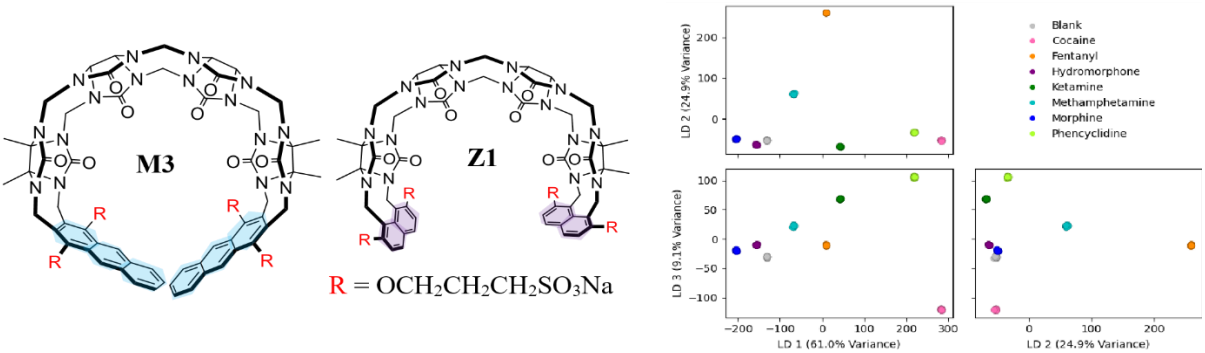


Figure 1. Naturally fluorescent aCB[n] containers **M3** and **Z1** can "fingerprint" drugs of abuse.

References

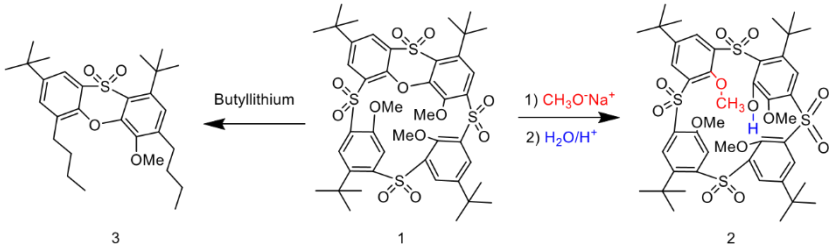
1. A.I. Lazar, F. Biedermann, K.R. Mustafina, K.I. Assaf, A. Hennig, W.M. Nau, *J. Am. Chem. Soc.* **2016**. *39*, 13022–13029.
2. E. Shcherbakova, B. Zhang, S. Gozem, T. Minami, P.Y. Zavalij, L. Isaacs, P. Anzenbacher, *J. Am. Chem. Soc.* **2017**. *42*, 14954–14960.
3. S. Murkli, J. Klemm, D. King, P. Y. Zavalij, L. Isaacs, *Chem. Eur. J.* **2020.** *26*, 15249-15258.

P12 Synthesis and Derivatization of Oxidized Thiacalixarenes

Mamleev K.,[a] Eigner V.,[b] Lhoták P.[a]

[a] *Department of Organic Chemistry,* [b] *Department of Solid State Chemistry, University of Chemistry and Technology, Prague (UCTP), Technická 5, 166 28 Prague 6, Czech Republic.*
E-mail: [a] mamleev@vscht.cz; [b] lhotakp@vscht.cz

Thiacalixarenes, the members of calixarene family, possess many unusual properties if compared with parent "classical" calixarenes. One of the most important features is the oxidation of sufide bridges, which changes both the complexation properties and the overall reactivity of the molecule. However, oxidation takes place not only on the sulfur atoms as documented by the formation of spiro derivatives in the reaction of thiacalixarene with chloramine-T. Moreover, subsequent treatment with hydrochloric acid produces an unusual phenoxathiin-based macrocyclic system.[1,2]



3 1 2

Scheme 1. *O*-nucleophile attack and the cleavage of **1** under the influence of *C*-nucleophile.

Previous studies have revealed that *O*-nucleophile attack cleaves the Ar-O-Ar bond in the middle of the phenoxathiin cycle. The reaction of sodium methoxide with phenoxathiin derivative **1** formed a new product **2**. Surprisingly, the application of *C*-nucleophiles (represented by butyllithium) led to completely different reaction pathway (Scheme 1).[3] Hence, our project aims at the cleavage of the phenoxathiin-based calixarene under the influence of various *C*-nucleophiles. The results and possible cleavage mechanisms will be discussed.

This research was supported by Czech Science Foundation (20-08667S) and by Specific University Research (A2 FCHT 2022 073).

References

1. J. Mikšátko, V. Eigner, H. Dvorakova, P. Lhotak, *Tetrahedron Letters* **2016**, *57*, 3781-3784.
2. T. Landovský, H. Dvořáková, V. Eigner, M. Babor, M. Krupička, M. Kohout, P. Lhoták, *New Journal of Chemistry* **2018**, *42*, 20074-20086.
3. T. Landovský, V. Eigner, M. Babor, M. Tichotová, H. Dvořáková, P. Lhoták, *Chemical Communications* **2020**, *56*, 78-81.

P13 Anion Binding by Fluorescent Hexahomotrioxacalix[3]arene Receptors

Marcos P.M.,[a,b] Miranda A.S.,[a,c] Ascenso J.R.,[d] Berberan-Santos M.N.[c]

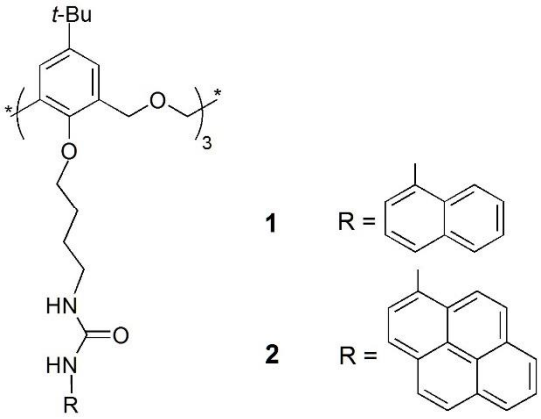
[a] CQE, FCUL, Edifício C8, 1749-016 Lisboa, Portugal; [b] FFUL, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal; [c] IBB, IST, Av. Rovisco Pais, 1049-001 Lisboa, Portugal; [d] CQE, IST, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.

E-mail: pmmarcos@fc.ul.pt

Anions play essential roles in biological systems, as well as in environmental and industrial processes.[1] Their recognition by receptors based on calixarenes continues to attract much attention. The incorporation of urea units have been intensively studied since these receptors use NH groups as H-bond donors to interact with the anions. Furthermore, calixarenes having optical sensing ability for different types of analytes have been developed, and fluorescence spectroscopy has been increasingly used for ion detection, owing to its high sensitivity and simplicity.[2]

Following our previous studies on anion binding by (thio)ureido-homooxacalixarenes,[3-5] we have extended those studies to fluorescent hexahomotrioxacalix[3]arenes.

This work reports the anion binding properties of two fluorescent receptors (**1** and **2**) based on hexahomotrioxacalix[3]arenes bearing naphthyl- or pyrenyl-urea groups on the lower rim via a butyl spacer. The anion binding was studied by NMR, UV-Vis absorption and fluorescence titrations in different solvents. The thermodynamics of complexation was also determined in acetonitrile.



Authors thank *Fundação para a Ciência e a Tecnologia*, Project UIDB/00100/2020.

References

1. P. A. Gale, E. N. W. Howe, X. Wu, *Chem.* **2016**, *1*, 351.
2. R. Kumar, A. Sharma, H. Singh, P. Suating, H. S. Kim, K. Sunwoo, I. Shim, B. C. Gibb, J. S. Kim, *Chem. Rev.* **2019**, *119*, 9657.
3. A. S. Miranda, D. Serbetci, P. M. Marcos, J. R. Ascenso, M. N. Berberan-Santos, N. Hickey, S. Geremia, *Front. Chem.* **2019**, *7*, Article 758.
4. A. S. Miranda, P. M. Marcos, J. R. Ascenso, M. N. Berberan-Santos, R. Schurhammer, N. Hickey, S. Geremia, *Molecules* **2020**, *25*, 4708.
5. F. A. Teixeira, J. R. Ascenso, P. J. Cragg, N. Hickey, S. Geremia, P. M. Marcos, *Eur. J. Org. Chem.* **2020**, 1930.

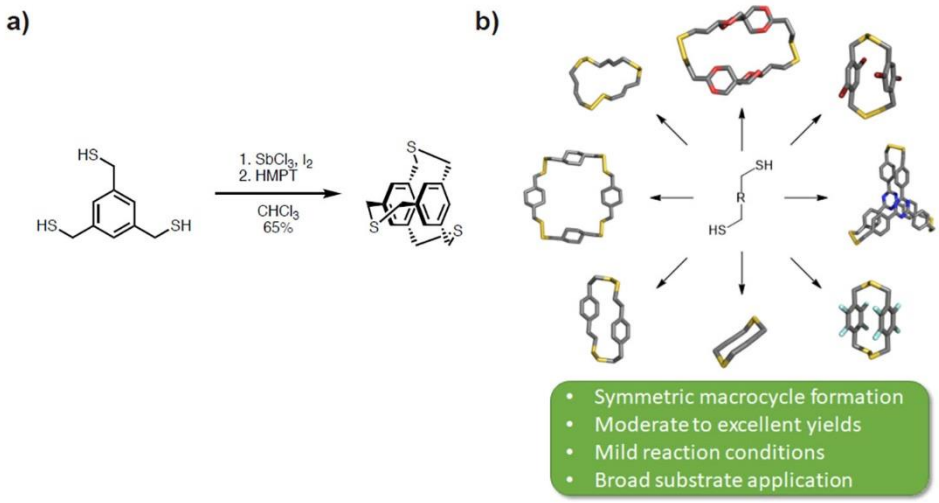
P14 Expanding the Scope of Pnictogen-Assisted Self-Assembly and Self-Sorting

Mayhugh J. T.,[a] Zocchi L. J.,[a] Davis W. A., Trubenstein H. J., Demachkie I. S.,[a] Zakharov L. N.,[c] Shear S. A.,[*b] Johnson D. W.[a]

[a] *Department of Chemistry & Biochemistry and Materials Science Institute, University of Oregon, 97403-1253 Eugene, OR, USA;* [b] *Lawrence Livermore National Laboratory, 7000 East Avenue, 94550-9234 Livermore, CA, USA* [c] *Center for Advanced Materials Characterization in Oregon (CAMCOR), University of Oregon, 97403 Eugene, OR, USA.*

E-mail: jmayhugh@uoregon.edu; lzocchi@uoregon.edu; wad@uoregon.edu

Cyclophanes are a fundamentally interesting class of compounds that host a wide range of unique and emergent properties. However, synthesis of complex and/or functionalized cyclophanes can often suffer from harsh reaction conditions, long reaction times, and sometimes low yields using stepwise methods. We have previously reported an efficient, high-yielding, metalloid-directed self-assembly method to prepare disulfide, thioether, and hydrocarbon cyclophanes and cages that feature mercaptomethyl-arenes as starting materials (figure 1a).[1] Herein, we present the synthesis of 24 new disulfide and thioether assemblies that expand this high yielding self-assembly method to a wide breadth of macrocycles and cages with diverse structures. Remarkably, the high-yielding, efficient syntheses still proceed under dynamic covalent control using electron-deficient, heteroaryl, cycloalkyl, spiro, and even short alkenyl/alkynyl substrates (figure 1b);[2] moreover, by self-sorting multiple building blocks, we can form asymmetric disulfide macrocycles and cages that are synthetically unachievable with conventional kinetic pathways.[3]



References

1. M. S. Collins, M. E. Carnes, B. P. Nell, L. N. Zakharov, D. W. Johnson, *Nat. Chem*. **2016**, *7*, 11052.
2. T. A. Shear, J. T. Mayhugh, L. J. Zocchi, I. S. Demachkie, H. J. Trubenstein, L. N. Zakharov, D. W. Johnson, *Eur. J. Org. Chem.* **2022**, *In Press*.
3. J. T. Mayhugh, W. A. Davis, L. J. Zocchi, H. J. Trubenstein, L. N. Zakharov, D. W. Johnson, *Manuscript in prep.*

P15 Novel Silica-Bound Supramolecular Chromatographic Stationary Phases

Mekapothula S.R.,[a] Wonanke A.D.D.,[a] Addicoat M.A.,[a] Boocock D.J.,[b] Cragg P.J.,[c] Wallis J.D.,[a] and Cave G.W.V.[a]

[a] Nottingham Trent University, School of Science and Technology, Clifton Lane, Nottingham, UK; [b] The John van Geest Cancer Research Centre, School of Science and Technology, Clifton Lane, Nottingham, UK; [c] School of Pharmacy and Biomolecular Science, Huxley Building, University of Brighton, Brighton, UK.

E-mail: subba.mekapothula@ntu.ac.uk

A novel co-pillar[4+1]arene incorporating bromo-octyl substituents has been synthesized for the first-time using microwave irradiation with high yield (88%) and subsequently bound to the surface of chromatographic silica particles. The resulting new stationary phase has been successfully utilized to separate all xylene isomers *via* the flash column chromatography technique.[1] To demonstrate the versatility of this new class of stationary phases, a silica immobilized co-pillar[4+1]arene supramolecular cavitand has been designed in-silico using host-guest binding energy studies, and realized experimentally to selectively interact with a range of peptides *via* their morphology and amino acid functionalities. The new computationally designed column demonstrates superior separation of five peptides (15-20 residues) compared to a traditional RP-C_{18} LC-MS/MS stationary phase.[2]

A silica-bound *C*-butylpyrogallol[4]arene chromatographic stationary phase was also prepared to evaluate both the preparative and analytical scale chromatographic separation of C_{60} and C_{70} fullerenes in reverse phase mode *via* flash column chromatography and HPLC. The two fullerenes were separated on this phase by size-selective molecular recognition as postulated from our in-silico studies.[3]

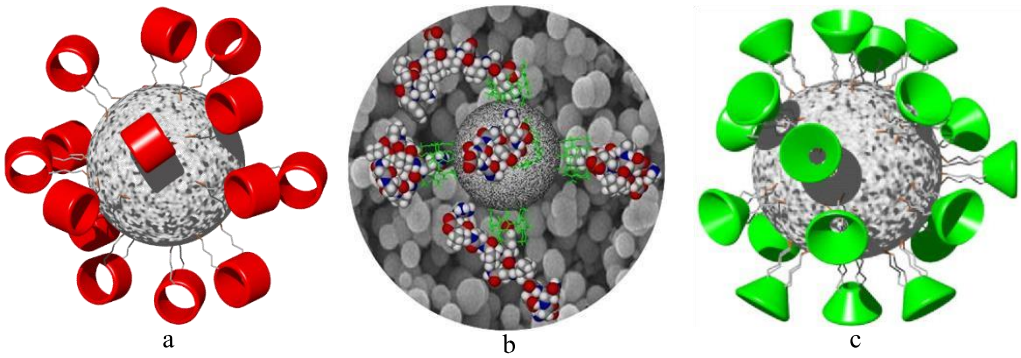


Figure 1. Co-pillar[4+1]arene bound silica flash column (a), UPLC (b), and *C*-butylpyrogallol[4]arene stationary phase

References

1. S. Mekapothula, M. A. Addicoat, D. J. Boocock, P. Cragg, J. D. Wallis and G. W. V. Cave, *Chem. Commun*. 2020, **56**, 1792-1794.
2. S. Mekapothula, A. D. D. Wonanke, M. A. Addicoat, D. J. Boocock, J. D. Wallis and G. W. V. Cave, *New J. Chem.*, 2021, **45**, 141-146.
3. S. Mekapothula, A. D. D. Wonanke, M. A. Addicoat, D. J. Boocock, J. D. Wallis, and G. W. V. Cave, *Int. J. Mol. Sci.*, 2021, **22**, 5726.

P16 Redox-active calix[6]arene funnel complexes

Nyssen N.[a,b], Aoun P.[a], Zhurkin F.[a], Jabin I[b], Reinaud O.[b]

[a] *Université de Paris Cité, Laboratoire de Chimie et de Biochimie Pharmacologiques et Toxicologiques, CNRS UMR 8601, 45 rue des Saints Pères, 75006 Paris, France ;* [b]*Université libre de Bruxelles (ULB), Laboratoire de Chimie Organique, Avenue F.D. Roosevelt 50, CP160/06, B-1050 Brussels, Belgium.*
E-mail: nicolas.nyssen@ulb.be

In Nature, there is a class of metallo-enzymes active in redox processes that present in their active site a phenol (Tyr) or quinone residue in the vicinity of the metal ion.[1] The role of the cofactor is to facilitate proton-coupled electron transfers. Inspired by Nature, we developped a strategy consisting of associating a transition metal ion to phenol or quinone moieties under the supramolecular control of a funnel-shaped calix[6]arene macrocycle. This unique combination mimics the cavity found in these metallo-enzymes (Fig. 1). The ultimate goal is to obtain a molecular electrocatalysts prone to multi-proton coupled to multi-electron transfers, such as those involved for CO_2 reduction.
We previously described calix[6]arene-based receptors capped by TREN [tris(2-aminoethyl)amine] and TMPA [tris(2-pyridylmethyl)amine] units.[2] The tripodal aza cap mimics the polyhistidine site found in metallo-enzymes, whereas the calix macrocycle plays the role of funnel for guest-ligands, controlling the metal ion 2nd and 3rd coordination spheres at remote distance.[3] Here, we will report the synthesis and characterization of new Zn^{II} and Co^{II} complexes. These metal complexes differ from each other by the presence of three anisole, phenol, or quinone moieties in the cavity surrounding the metal ion. Their host-guest properties will be compared and preliminary data relative to their redox activity toward CO_2 reduction will be presented.

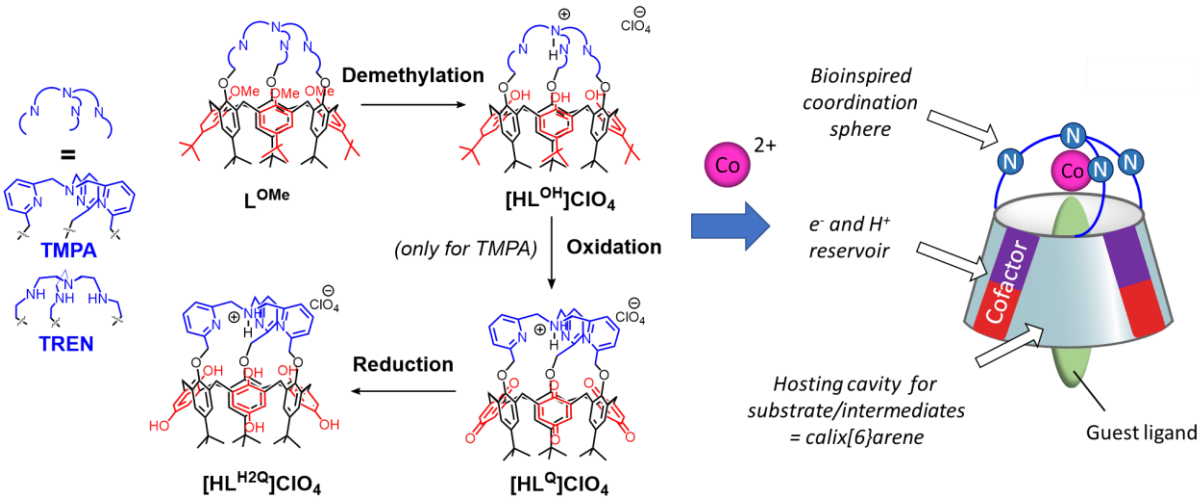


Figure 1. Synthesis of the calix[6]arenes ligands with different 2nd and 3rd coordination spheres and schematized calix[6]arene platform associating transition metal, organic redox cofactor and funnel-shape chamber for hosting and catalysis.

References

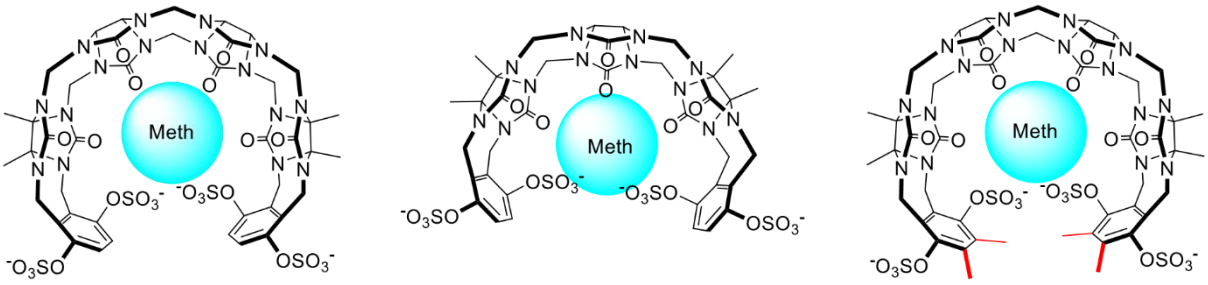
1. N. M. Okeley, W. A. van der Donk, *Chemistry & Biology* **2000**, *7*, 159–171.
2. a) I. Jabin, O. Reinaud, *J. Org. Chem.* **2003**, *68*, 3416-3419; b) X. Zeng, D. Coquière, A. Alenda, E. Garrier, T. Prangé, Y. Li, O. Reinaud and I. Jabin, *Chemistry – A European Journal* **2006**, *12*, 6393-6402.
3. N. Le Pou l, Y. Le Mest, I. Jabin, O Reinaud, *Acc. Chem. Res.* **2015**, *48*, 2097–2106.

P17 Development of Sulfated Acyclic CB[*n*] Type Receptors as a Sequestering Agent for Drugs of Abuse

Perera S., and Isaacs L.

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, United States.
E-mail: suvenika@umd.edu

The binding properties of acyclic cucurbit[*n*]urils, (CB[*n*]'s) with drugs of abuse has shown promising results to incorporate them as a treatment for drug overdose. Previous studies in the Isaacs group have demonstrated the positive impact in the binding of acyclic CB[*n*]s, when the SO_3^- moieties are positioned as near the ureidyl carbonyl portals as possible.[1] In this poster, I build on these results by synthesizing a new sulfated acyclic CB[*n*] receptor (**Me$_4$TetM0**), to study the influence of adding methyl groups to the aromatic side-walls in addition to placing the SO_3^- moieties near the portals, upon binding with a panel of drugs of abuse.[2] The binding of **Me$_4$TetM0** towards drugs of abuse has been investigated using ^{1}H NMR titration and isothermal titration calorimetry and was compared with the results from two other hosts (**TetM0 and TriM0**). **Me$_4$TetM0** shows very good binding affinity towards the drugs of abuse but is slightly less potent than **TetM0**. **TriM0** generally shows lower binding affinity compared to **TetM0** and **Me$_4$TetM0**. The selectivity of **TetM0** vs. **Me$_4$TetM0** for drugs such as methamphetamine, fentanyl, MDMA and mephedrone range from 4.6 to 9.7. Even though the methyl groups attached to **Me$_4$TetM0** increases the cavity size and the hydrophobic interactions, the results indicate that **TetM0** contains the proper cavity size for methamphetamine and fentanyl. In vivo studies performed using **TetM0** demonstrated the ability to control the hyperlocomotion induced by methamphetamine in mice.



TetM0•Meth
$K_a = 2.49 \times 10^6\ M^{-1}$

TriM0•Meth
$K_a = 3.44 \times 10^3\ M^{-1}$

Me$_4$TetM0•Meth
$K_a = 2.57 \times 10^5\ M^{-1}$

Figure 1. Representations of A) TetM0●Meth complex; B) TriM0●Meth complex; C) Me$_4$TetM0●Meth complex.[2]

References

1. X. Lu, S. A. Z. Ndendjio, P. Y. Zavalij, L. Isaacs, *Org. Lett*. **2020**, *22*, 4833–4837.
2. A. T. Brockett, C. Deng, M. Shuster, S. Perera, D. DiMaggio, M. Cheng, S. Murkli, V. Briken, M. R. Roesch, L. Isaacs, *Chem. Eur. J*. **2021**, *27*, 17476-17486.

P18 Quinoxaline Cavitands for PFAS Removal from Water

Pinalli R., Dalcanale E., Pedrini A.

Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Italy.
E-mail: roberta.pinalli@unipr.it

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic, fluorinated compounds that have been widely used for decades in industrial processes, firefighting foams and consumer products.[1] PFAS, nicknamed "forever chemicals", are highly persistent contaminants that can accumulate in the environment and living organisms. Human exposure to these compounds has been linked to a range of diseases including cancer, obesity, and endocrine disruption.[2-3] Even if officially banned or restricted because of their toxic, persistent and bioaccumulative effects, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) can still be found in water, and many smaller-chain PFAS are still in use, which toxicity is a concern. Few technologies are considered today to remove PFAS from water (especially PFOA and PFOS which are the most studied of these chemicals), namely activated carbon adsorption, ion exchange resins, and high-pressure membranes.[4] Recently, we have developed a polymeric membrane functionalized with quinoxaline-based cavitands for the removal of polycyclic aromatic hydrocarbons from water.[5] Quinoxaline cavitands (Figure 1) are synthetic macrocycles presenting enforced cavities of molecular dimensions, which have been used as adsorbent materials for organic pollutants in water.[6] In particular, polymer adsorbents based on quinoxaline cavitands are effective in the uptake of chlorinated aromatic[7] and aliphatic hydrocarbons.[8] Two major factors contribute to their cavitand complexation properties in water: the hydrophobicity of the guest, which determines its affinity for the hydrophobic cavity, and shape complementarity. Here we show our recent studies about the possibility to use quinoxaline-based cavitands (Figure 1) at the solid-water interface for the efficient removal of PFAS from water.

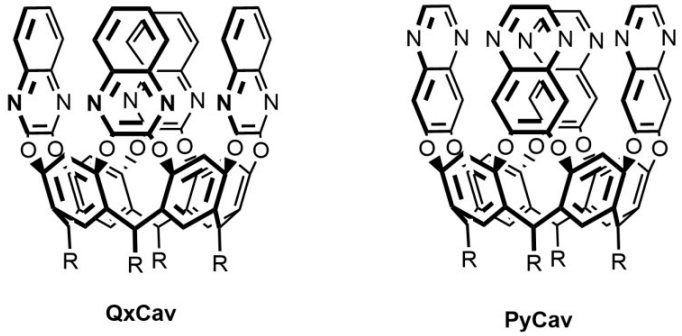


Figure 1. QxCav: quinoxaline cavitand; PyCav: pyrazine

References

1. E. Kissa: Fluorinated surfactants and repellents, 2nd ed.; CRC Press: Boca Raton, FL, 2001.
2. J. M. Braun, A.Chen, M. E. Romano, A. M. Calafat, G. M. Webster, K. Yolton, B. P.Lanphear. *Obesity* **2016**, *24*, 231.
3. V. Barry, A. Winquist, K. Steenland. *Environ. Health Perspect* **2013**, *121* (11–12), 1313.
4. https://www.epa.gov/sciencematters/reducing-pfas-drinking-water-treatment-technologies#:~:text=Activated%20carbon%2 0treatment%20is%20the,in%20drinking%20water%20treatment%20systems.
5. R. Pinalli, and E. Dalcanale et al. *Small* **2022**, *18*, 2104946.
6. a) E. Dalcanale, G. Costantini, P. Soncini, *J. Incl. Phenom. Mol. Recognit. Chem.* **1992**, *13*, 87. b) E. Dalcanale, J. Hartmann, Sens. Actuators B. Chem. 1995, 24, 39. c) E. Dalcanale et al., *Sensors Actuators B* **1996**, *35*, 154.
7. E. Dalcanale, R. Pinalli et al., *Sens. Actuators B* **2018**, *276*, 340.
8. L. P. Skala, A. Yang, M. J. Klemes, L. Xiao, W. R. Dichtel, *J. Am. Chem. Soc.* **2019**, *141*, 13315.
9. F.-U. Rahman, H.N. Feng, Y. Yu. *Org. Chem. Front.* **2019**, *6*, 998.

P19 Organocatalysis in Aqueous Media

Priyanka P., Ismaiel Y.A., and Gibb B.C.

Tulane University, New Orleans, Louisiana, United States.
E-mail: pprusty@tulane.edu

Aryl iodides are excellent precursors in organic synthesis, medicine and biochemistry. Iodine being the least reactive halogen towards electrophilic substitution, direct iodination of aromatic compounds is difficult. As a result, most methods utilize harsh reaction procedures involving combinations of strong Bronsted and Lewis acids and strong oxidizers.[1,2] Unsurprisingly, mild iodination processes are keenly saught.[3]

One aim of our group is the development of novel organo-catalysts, and during recent studies we identified an efficient iodination process that occurs under mild conditions (water, rt, pH ~ 7). The hosts themselves are air-stable, non-toxic and easy to handle, which make them attractive tools for green chemistry. Preliminary investigations have focused on relatively active aromatics such as anisole, and spectroscopic and crystallographic data suggest the formation of interhalogen (eg., I-Cl) as key for iodination (Figure 1). We will summarize our latest findings, focusing on our studies exploring the scope and mechanisms of the reaction, and how the nature of the host can affect reactivity.

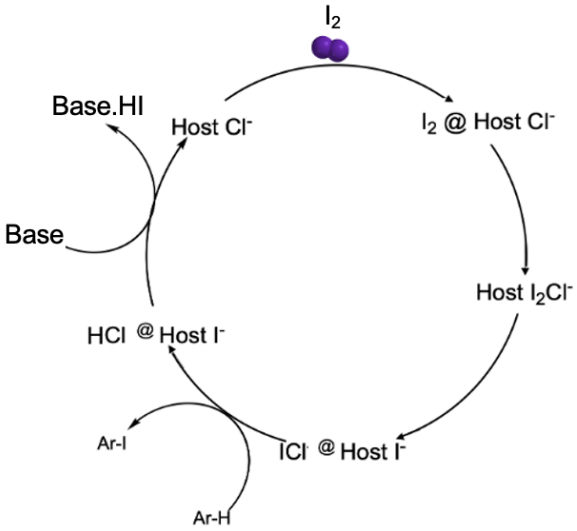


Figure 1. Possible mechanism of iodination of aromatic compounds.

References

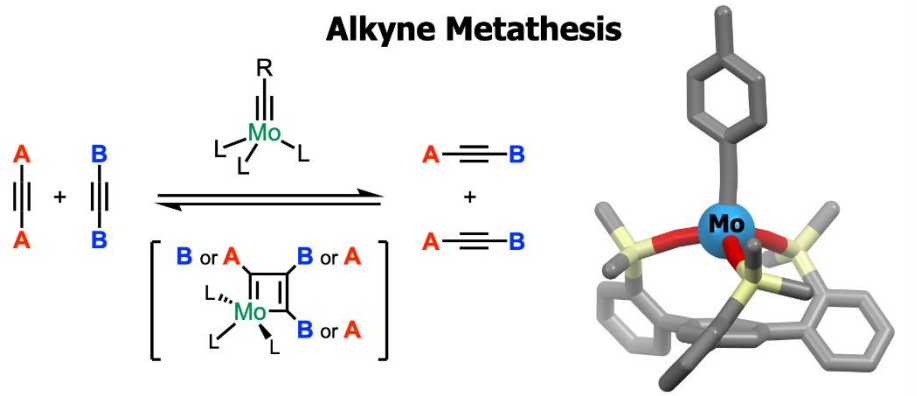
1. S. Bahrami-Nasab, A. R. Pourali, S. Mohamad Reza Nazifi, *National Academy Science Letters* **2014,** *38* (1), 45-48.
2. S. Stavber, M. Jereb, M. Zupan, *Synthesis* **2008,** *2008* (10), 1487-1513.
3. X. Xiong, Y. Y. Yeung, *Angew. Chem. Int. Ed. Engl.* **2016,** *55* (52), 16101-16105.

P20 Alkyne Metathesis Catalysts with Podand and Macrocyclic Ligands

Riman-Tanha S., Njoroge S., Stewart M. L., Napier S. E., Cao K. T., Lee S.

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.
E-mail: stanha2@lsu.edu

Alkyne metathesis[1] is a powerful synthetic method to prepare macrocycles and cage compounds in high yields. The best performing catalysts[2] are mostly based on Mo(VI)-alkylidyne complexes with three anionic ligands. However, they still suffer from limited stability against moisture, protic/polar solvents, and reactive substrates. Here, we present the synthesis and performance of various Mo-based alkyne metathesis catalysts based on podand[3,4] and macrocyclic ligands.



References

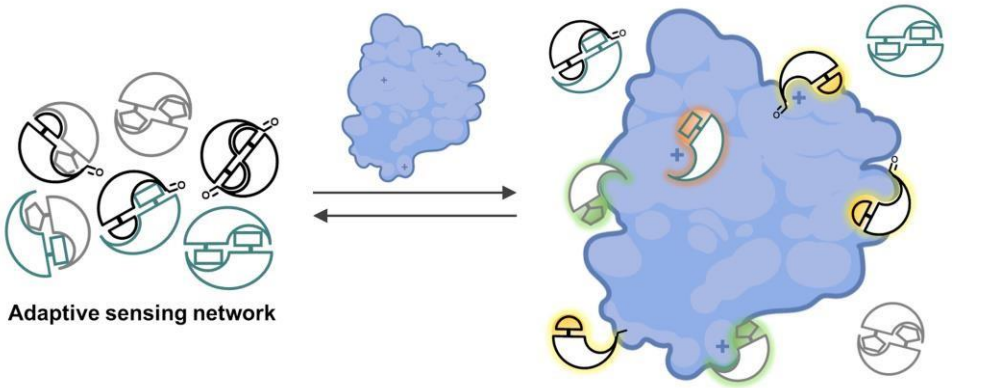
1. A. Furstner, *Angew. Chem. Int. Ed*. **2013**, *52*, 2794-2819.
2. Y. Ge, Y. Hu, G. Duan, Y. Jin, W. Zhang, *Trends in Chemistry* **2022**, DOI 10.1016/j.trechm.2022.03.004.
3. R. R. Thompson, M. E. Rotella, P. Du, X. Zhou, F. R. Fronczek, R. Kumar, O. Gutierrez, S. Lee, *Organometallics* **2019**, *38*, 4054-4059.
4. R. R. Thompson, M. E. Rotella, X. Zhou, F. R. Fronczek, O. Gutierrez, S. Lee, *J. Am. Chem. Soc.* **2021**, *143*, 9026-9039.

P21 Systems Chemistry for Sensing: Multi-Responsive Arrays and Adaptive Networks

Selinger A. J., Beatty M. A., Hof F.

University of Victoria, Department of Chemistry, Victoria, British Columbia, Canada.
E-mail: allisonselinger@uvic.ca

We have previously reported DimerDyes, a family of self-assembling calixarene chemosensors that function through a unique disassembly-driven sensing mechanism.[1] DimerDyes form self-assembled dimers that persist in biological solutions. These sensors disassemble in the presence of hydrophobic and cationic analytes, providing a chemometric response. Using an array of these individual sensors we have achieved detection and discrimination of closely related illicit drugs and their metabolites at low micromolar concentrations.[2] Here we report new analogs with both colour changing and turn-on fluorescence properties, varying in fluorescence functionality and binding pocket size. Building on this sensing system, we have recently combined sensors in solution to form an adaptive one-pot sensing network that can discriminate closely related protein homologs. This dynamic network acts as a multi-responsive system to provide data-rich optical outputs for complex biological analytes.



References

1. M. A. Beatty, J. Borges-González, N. J. Sinclair, A. T. Pye, F. Hof, *J. Am. Chem. Soc.* **2018**, *140*, 10, 3500-3504.
2. M. A. Beatty, A. J. Selinger, Y. Li, F. Hof. *J. Am. Chem. Soc.* **2019**, *141*, 42, 16763-16771.

P22 Easy and Selective Method for Desymmetrization of Tetrabrominated Calixarenes in Different Conformations

Surina A.,[a] Eigner V.,[b] M. Krupička and Lhoták P.[a]

[a] Department of Organic Chemistry, University of Chemistry and Technology, Prague (UCTP), Technická 5, 166 28 Prague 6, Czech Republic; [b] Department of Solid State Chemistry, UCTP, 166 28 Prague 6, Czech Republic.

E-mail: Surinaa@vscht.cz

Dessymetrization of tetrasubstituted derivatives would be very useful synthetic tool in calix[4]arene chemistry. Unfortunately, the only known example is the reaction of a tetrabromo derivative with butyllithium, in which two opposing bromine atoms react preferentially to give the corresponding disubstituted product.[1] While this reaction has been described for the *cone* conformer, to our surprise, this promising approach has never been tested with any other conformation to determine its general applicability in calix[4]arene chemistry. Moreover, to the best of our knowledge, no one has yet even attempted to explain the surprising selectivity of the reaction.

The first part of this work is focused on the preparation of dibromo derivatives and distannio derivatives of calix[4]arene in the *cone*, *1,3-alternate* and *partial cone* conformations selectively obtained from the tetrahalogenated calixarene derivatives. In the second part, stannio substrates were used to study Stille's type cross-coupling reactions. As shown in this work, the products of these reactions can be applied for construction of more complex receptors.

To shed more light on the above-described unexpected selectivity we have performed theoretical calculations with the *cone* conformer as the model compound.

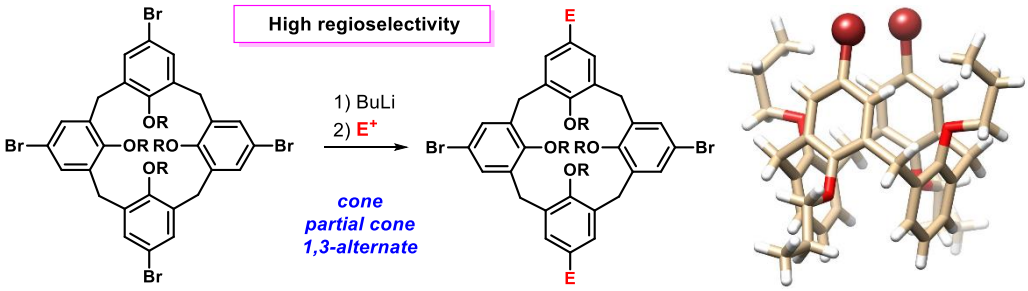


Figure 1. Dessymetrization of tetrabromocalix[4]arenes; the X-ray structure of disubstituted product in the *1,3-alternate* conformation

This research was supported by Czech Science Foundation(20-07833S) and by Specific University Research (A2 FCHT 2022 065).

References

1. M. Larsen, M. Jørgensen, *J Org. Chem.* **1996**, *61* (19), 6651-6655.

P23 Beyond Hofmeister Effects: Does Halogen Bonding Play a Role in Protein Precipitation with Trihaloacetates?

Tran T.H., and Gibb B.C.

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, United States.
E-mail: ttran25@tulane.edu

Trichloroacetate is a well-known, 'super-precipitator' of proteins.[1] However, the mechanism by which it induces precipitation is not yet understood. As part of our program investigating this, we are exploring the different non-covalent interactions that trihaloacetates (THAs) can form with co-solutes. One possibility is that THAs can act as halogen bond (XB) donors to amide carbonyl donors of proteins.[2,3] To explore this possibility in models, we are using a combination of isothermal titration calorimetry (ITC), nuclear magnetic resonance (NMR) spectroscopy, and in silico simulations to examine the interactions between THAs and the rim of cucurbituril hosts. In parallel, we are carrying out similar studies with THAs and model hosts to gain an understanding of the interactions between these anions and the non-polar regions/pockets of proteins. We will discuss these sub-projects, as well as our recent NMR and differential scanning calorimetry (DSC) studies probing the effects of the interactions between THAs and the protein Ubiquitin.

References

1. L. Koontz, *Methods Enzymol*. **2014**, 541, 3-10.
2. G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *J. Chem. Rev.* **2016**, 116, 2478–2601.
3. P. Metrangolo, T. Pilati, G. Resnati, *Cryst. Eng. Comm.* **2006**, 8, 946-947.

P24 Anion Affinity of *N*-Terminal α-Synuclein$_{15}$ Peptides

Wang R., Gibb B.C.

Department of Chemistry, Tulane University, New Orleans, 70118, United States.
E-mail: rwang20@tulane.edu

α-Synuclein (α-Syn) is an intrinsically disordered protein linked to the pathogenesis of Parkinson's disease (PD) by its misfolding, aggregation, and accumulation in Lewy bodies; the characteristic amyloids of PD.[1] The imperfect N-terminal repeat sequence XKTKEGVXXXX has been regarded as a key factor in its aggregation and fibril formation.[2,3] A central theme of the group's research is understanding the non-covalent interactions between proteins/peptides and in situ ions, and how these can induce aggregation of the biomacromolecule. For example, we will report here on our studies with a N-terminal peptide of α-Syn (1MDVFMKGLSKAKEGV15, Figure 1), as well as the corresponding triple arginine mutant 1MDVFMRGLSRAREGV15. A series of NMR techniques 1H-15N/13C HSQC, NOESY, ROESY, TOCSY and COSY is utilized to obtain an understanding of the interactions of these peptides with a range of anions, and titration plotting is used to show the binding affinity of peptide at various amino acids. Complementing these techniques, CD spectroscopy is utilized to track conformational changes of the peptide in response to salts and pH. In addition to these experiments, molecular dynamic (MD) simulations to evaluate the anion-peptide interactions will also be described. These will provide atomistic-level insights into solvation and binding, as well as any significant peptide structural changes. Taken together, these studies will allow us to map anion-peptide interactions to aggregation predisposition, and hence identify structural and environmental factors key to amyloid genesis.

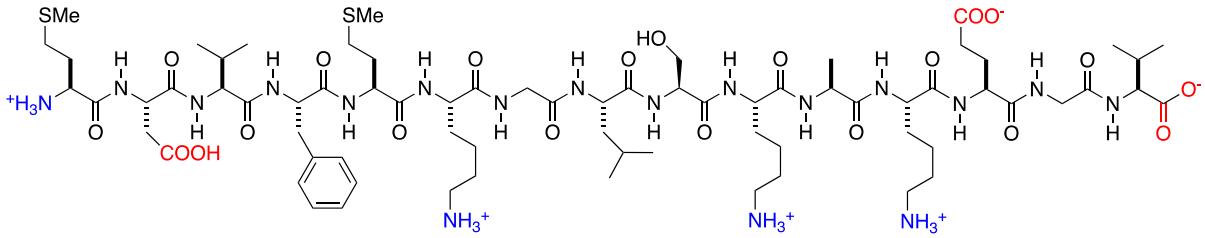


Figure 1. Chemical structure of wild-type α-Syn.

References

1. A.L. Fink, *Acc. Chem. Res.* **2006**, *39,* 628-34.
2. J. C. Kessler, J.-C. Rochet, P. T. Lansbury, *Biochemistry*, **2003**, *42*, 672-678.
3. U. Dettmer, A. J. Newman, D. Selkoe, *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 9596-601.

P25 Large-Scale, Chromatography-Free Ethoxypillar[6]arene Synthesis

Wilson C. R., Chen E. F. W., Puckett A. O., Hof F.

University of Victoria, Department of Chemistry, Victoria, British Columbia, Canada.
E-mail: crwilson@uvic.ca

Pillar[n]arenes are a family of macrocycles that have quickly become important in supramolecular chemistry. Pillar[5]arene[1] is the most commonly studied pillar[n]arene, however its small internal cavity limits its applications. The larger pillar[6]arene[2] is a highly desired host. The sulfated analog (PillarMaxQ) has been shown to bind biologically relevant guests with picomolar affinity.[3] Ethoxypillar[6]arene (EtOP6) is a key intermediate in the formation of many pillar[6]arene derivatives. Quick and easy access to this initial scaffold is key for new functionalization methods and further applications. Access to this analog however is currently limited, as the formation of pillar[6]arene is disfavored in the cyclization reaction, predominantly resulting in the less strained pillar[5]arene. Alkoxy-protected pillar[6]arenes are generally made through a solvent-templated Friedel–Crafts cyclization. While there are many reported methods to make ethoxypillar[6]arene, they have significant downfalls. They are not ring-size selective, they require unusual protecting groups, and/or they are run on small scales. Published methods require difficult separations of pillar[5]arene and other pillar[n]arene byproducts. To overcome these shortcomings, we developed a method that exclusively makes ethoxypillar[6]arene, thus avoiding the need for chromatographic purification. Our method can be run on scales from 1 to 40 grams. Easier access to ethoxypillar[6]arene will help enable new host-guest chemistry, functionalization methods and novel derivatives of pillar[6]arene.

References

1. T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi, Y. Nakamoto, *J. Am. Chem. Soc.* **2008**, *130*, 5022-5023.
2. D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang, H. Meier, *Angew. Chem. Int. Ed.* **2009**, *48*, 9721-9723.
3. W. Xue, P. Y. Zavalij, L. Isaacs, *Angew. Chem. Int. Ed.* **2020**, *59*, 13313-13319.

P26 Magneto-Structural Investigations of Calix[4]arene-Supported Metal Clusters

Wilson L. R. B.,[a] Dalgarno S. J.,[b] Brechin E. K.[a]

[a] *School of Chemistry, University of Edinburgh, Edinburgh, Scotland, EH9 3FJ, UK;* [b] *Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, Scotland, EH14 4AS, UK.*
E-mail: s1503785@sms.ed.ac.uk

The use of calix[4]arenes (C[4]s) in supramolecular coordination chemistry promises to yield a variety of polymetallic clusters of paramagnetic ions, due to their conformational versatility and ease of synthetic modification. The ability to link two C[4]s directly, creating the 2,2'-biscalix[4]arene (BisC[4]) ligand with 8 phenolic O-atoms in close proximity, offers an appealing foundation for magneto-structural investigations. At present, various 3*d*, 4*f* and 3*d*/4*f* polymetallic clusters exhibiting interesting magnetic properties, nuclearities and topologies have been assembled, suggesting many novel clusters should be readily accessible.[1] Current work involves extending coordination across the 3*d* and 3*d*/4f series'.

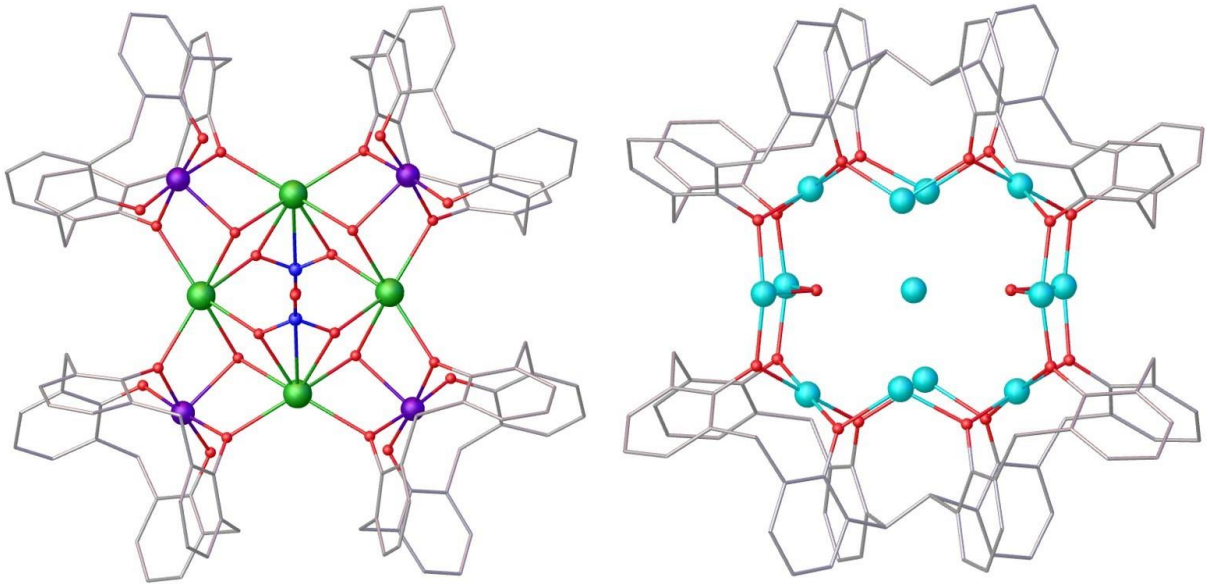


Figure 1. Examples of TBC[4]-supported (left) and BisTBC[4]-supported (right) polymetallic complexes.

References

1. a) G. Karotsis, M. Evangelisti, S. J. Dalgarno, E. K. Brechin, *Angew. Chem. Int. Ed.* **2009**, *48,* 9928-9931; b) R. McLellan, M. A. Palacios, C. M. Beavers, S. J. Teat, S. Piligkos. E. K. Brechin, S. J. Dalgarno, *Chem. Eur. J.* **2015**, *21*, 2804-2812.

P27 Towards the Design and Synthesis of Novel Amino Acid Functionalized Deep Cavity Cavitands

Wyshel T.S., Gibb C.L.D, and Gibb B.C.

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118 United States.
E-mail: twyshel@tulane.edu

Cavitands such as octa-acid **1** and positand **2** have been shown to form capsular complexes around non-polar guests in water; complexes that can be used to bring about novel separations,[1] and act as yocto-liter reaction vessels.[2, 3] Despite these advances, the formation of equivalent, chiral, cavitands has not been reported; despite the effects that chirality can have on such complexes or assemblies.[4] We will describe our ongoing efforts to form chiral versions of these hosts by decorating their exterior with amino-acids, for example octa-alanine **3**. We expect these unusual caviteins[5] to display enantioselective recognition properties, and will report on their synthesis and binding properties.

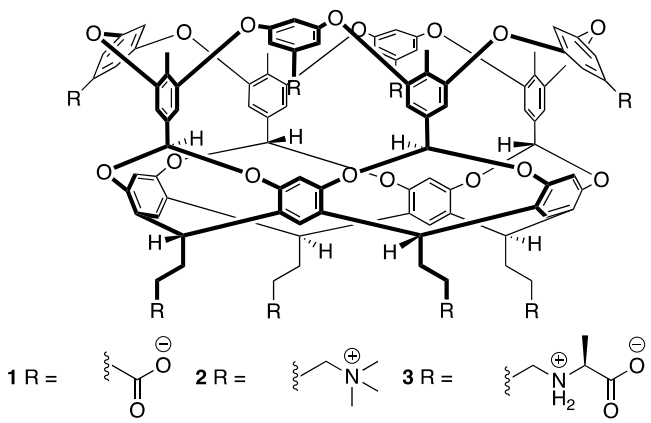


Figure 1. Cavitand hosts **1**-**3**

References

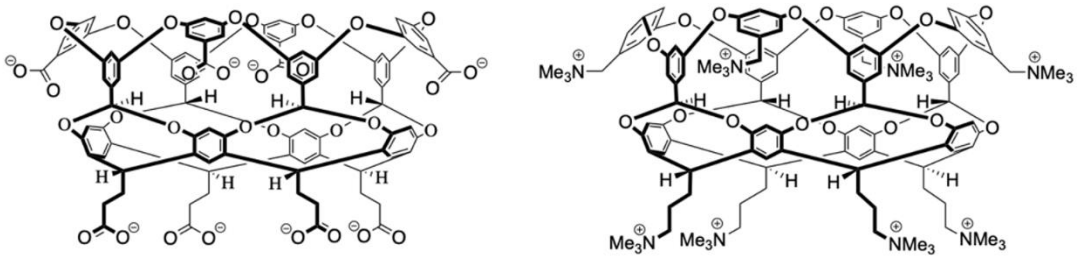
1. S. Liu, H. Gan, A. T. Hermann, S. W. Rick, B. C. Gibb, *Nat. Chem.* **2010,** *2*, 847-852.
2. W. Yao, K. Wang, Y. A. Ismaiel, R. Wang, X. Cai, M. Teeler, B. C. Gibb, *J. Phys. Chem. B* **2021,** *125*, 9333-9340.
3. K. Wang, X. Cai, W. Yao, D. Tang, R. Kataria, H. S. Ashbaugh, L. D. Byers, B. C. Gibb, *J. Am. Chem. Soc.* **2019,** *141*, 6740–6747.
4. A. Scarso, J. Rebek Jr., *Top. Curr. Chem.* **2006,** *265*, 1-46.
5. A. R. Mezo, J. C. Sherman, *J. Am. Chem. Soc.* **1999,** *121*, 8983-8994.

P28 Molecular Packing Within Water-Soluble Cavitands

Yujian X., Bruce C. G.

Department of Chemistry, Tulane University, New Orleans, Louisiana, 70118, United States.
E-mail: yxu24@tulane.edu

Octa-carboxylate **1** and positand **2** (Figure 1) are two key cavitands in the Gibb group;[1,2] eight charged groups ensure excellent water solubility, whilst the hydrophobic pocket can accommodate a range of guest molecules. Long chain thiols[3], alkanes,[4] to name a few, can be bound within the cavity of dimeric capsules formed by such hosts. We are interested in how the electrostatic potential field of the charged groups on the exterior of the capsules $\mathbf{1}_2$ and $\mathbf{2}_2$ can affect guests bound within their inner spaces. For example, long-range ion-ion interactions between the exterior charge groups and bound thiolates greatly affect the pKa of the corresponding thiol guests.[5] We will present our latest results investigating the extent to which ion-dipole interactions between the host (the ion) and guest (the dipole) can control guest conformation and reactivity. More specifically, we will report on the binding motif and physicochemical properties of several classes of flexible molecules that possess substantial dipoles.



1 **2**

Figure 1. octa-carboxylate **1** and oct-trimethylammonium (Positand; **2**).

References

1. C. L. D. Gibb, B. C. Gibb, *J. Am. Chem. Soc.* **2004**, 126, 11408−11409.
2. M. B. Hillyer, C. L. D. Gibb, P. Sokkalingam, J. H. Jordan, S. E. Ioup & B. C. Gibb, *Org. Lett.* **2016**, *18*, 4048−51.
3. K. Wang, X. Cai, W. Yao, D. Tang, R. Kataria, H. S. Ashbaugh, L. D. Byers, B. C. Gibb, *J. Am. Chem. Soc.* **2019**, *141*, 6740–6747.
4. S. Liu, D. H. Russell, N. F. Zinnel, B. C. Gibb, *J. Am. Chem. Soc.* **2013**, *135*, 4314−4324.
5. X. Cai, R. Kataria, B. C. Gibb, *J. Am. Chem. Soc.* **2020**, *142*, 8291-8.

P29 Functional FRET Antenna Based on a Heteromeric Parallel G-Quadruplex Scaffold

Zarandi M.A., Jayawickramarajah J.

Department of Chemistry, Tulane University, New Orleans, LA 70118, U.S.A.
E-mail: mzarandi@tulane.edu

In light harvesting systems including multiple chromophores, energy transfer between donor and acceptor is often explained by nonradiative Forster resonance energy transfer (FRET) mechanism. FRET efficiency depends on two important factors: distance and orientation between the donor and acceptor [1]. According to the FRET theory, the energy efficiency is inversely proportional to the donor-acceptor distance by the power of six [2].

G-quadruplexes are a higher-order structure of DNA and RNA that form in guanine-rich sequences with 3 or more consecutive guanine nucleotides and have a high melting temperature (~100˚C) [3]. Due to this feature, these nanostructures are an ideal choice for preparing scaffolds for nanophotonic application.

Photonic integrated circuits (PICs) are a new technology that supports many applications in which light has an important role. DNA nanotechnology has led to the development of elegant photonic architectures of increasing complexity. However, there is a gap in knowledge in terms of the development of effective antenna (light-harvesting) modules that are (a) compact, (b) have high-dye density, and (c) can be readily integrated with DNA nanostructures.

In this presentation, we will investigate a self-assembly strategy to construct heteromeric G-quadruplex nanostructures bearing fluorophores where the number of donor fluorophores can be modulated. These nanostructures contain a toehold part that can self-assemble to either a single complementary strand or other DNA based nanostructures (containing one or several acceptor fluorophores) to develop photonic FRET antennas. Steady-state fluorescence measurements will be conducted to assess and compare photophysical properties of each light harvesting antenna.

References

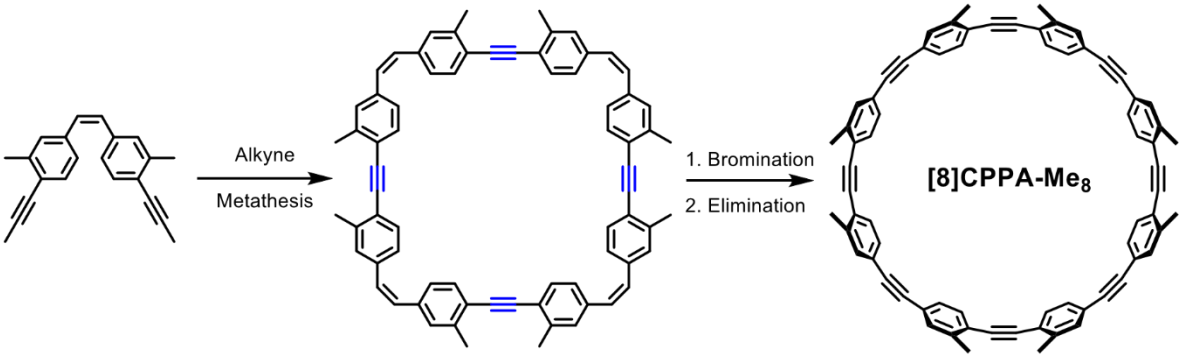
1. S. Hirashima, H. Sugiyama, S. Park, *The Journal of Physical Chemistry B* **2020**, *124*, 8794-8800.
2. I. Oh, H. Lee, T. W. Kim, C. W. Kim, S. Jun, C., Kim, H. Ihee, *Advanced Science* **2020**, *7*, 2001623.
3. S. Burge, G. N. Parkinson, P. Hazel, A. K. Todd, S. Neidle, *Nucleic Acids Res.* **2006**, *34*, 5402–5415.

P30 Synthesis of Cycloparaphenyleneacetylene Derivatives using Alkyne Metathesis

Zhou X., Herman R. J., LaFleur L., Lee S.

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.
E-mail: xzhou22@lsu.edu

Cycloparaphenyleneacetylene (CPPA) is a carbon nanohoop that has unique photophysical and supramolecular properties due to its curved aromatic structure and strained alkynes. CPPAs were previously prepared by macrocyclizations using irreversible coupling reactions. This often led to low yields of desired macrocycles and large amounts of undesired oligomers and polymers. By using alkyne metathesis, we were able to take advantage of Dynamic Covalent Chemistry and synthesize [3]CPP^{3}A, [3]CPP^{4}A and [3]CPP^{5}A nanohoops in high yields.[1,2] We further improved the method by combining Kawase and Oda's bromination/elimination[3] with alkyne metathesis. This allowed us to achieve a scalable synthesis of [8]CPPA derivatives.[4] Here, we also introduce a unique host-guest comlpex that involves the large central binding site of [8]CPPA.



References

1. S. Lee, E. Chenard, D. L. Gray, J. S. Moore, *J. Am. Chem. Soc.* **2016**, *138*, 13814-13817.
2. X. Zhou, R. R. Thompson, F. R. Fronczek, S. Lee, *Org. Lett.* **2019**, *21*, 4680-4683.
3. T. Kawase, H. R. Darabi, M. Oda, *Angew. Chem. Int. Ed.* **1996**, *35*, 2664-2666.
4. X. Zhou, H. Kwon, R. R. Thompson, R. J. Herman, F. R. Fronczek, C. J. Bruns, S. Lee, *Chem. Commun.* **2021**, 57, 10887-10890.

AUTHOR INDEX

IN-PERSON ATTENDANTS

A

Avram-Biton, Liat (Weizmann Institute of Science, Israel)

B

Badjić, Jovica (The Ohio State University, USA)

Baldini, Laura (Università di Parma, Italy)

Ballester, Pablo (Institute of Chemical Research of Catalonia (ICIQ), Spain)

Barboiu, Mihail (Institut Européen des Membranes, France)

Beltrami, Noah (Tulane University, USA)

Beyeh, Ngong Kodiah (Oakland University, USA)

Busschaert, Nathalie (Tulane University, USA)

C

Campbell, Cameron (Heriot-Watt University, UK)

Cohen, Yoram (Tel Aviv University, Israel)

Cvetnić, Marija (University of Zagreb, Croatia)

D

Dalcanale, Enrico (Università di Parma, Italy)

Davis, Willow (University of Oregon, USA)

de Mendoza, Javier (Institute of Chemical Research of Catalonia (ICIQ), Spain)

E

Elgrishi, Noémie (Louisiana State University, USA)

G

Gaeta, Carmine (University of Salerno, Italy)

Gale, Philip (The University of Sydney, Australia)

García-López, Victor (Louisiana State University, USA)

Gibb, Bruce (Tulane University, USA)

Gibb, Corinne (Tulane University, USA)

H

X

Z

VIRTUAL PRESENTERS