

# 2<sup>nd</sup> UBC – Tsinghua Joint Symposium on Modern Chemistry

Vancouver, Canada

August, 8<sup>th</sup> 2018



Lecture Room 102, 1<sup>st</sup> floor, Michael Smith Labs

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**8:45**      **REGISTRATION**

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**Opening Remarks****9:00**      The University of British Columbia (Prof. Michael O. Wolf)  
Tsinghua University (Prof. Huaping Xu)**MORNING SESSION I***Chair: Hongbin Li***9:20**      **Factoids about Tactoids: New Materials from  
Cellulose Nanocrystals**      P4  
Mark MacLachlan**9:45**      **Designed Synthesis and Chiroptical Response of  
Structurally Well-Defined Chiral Gold Clusters**      P6  
Liang Zhao**10:10**      **Photophysics and Photochemistry of Sulfur-Bridged  
Chromophores**      P8  
Michael O. Wolf**10:35**      **Coffee Break****MORNING SESSION II***Chair: Dongsheng Liu***11:00**      **Dynamic Chemistry of Selenium-containing Polymers**      P10  
Huaping Xu**11:25**      **Ordered Multiblock Nanofibers from Organic  
Electronic Materials**      P12  
Zac Hudson**11:50**      **Cobalt-Catalyzed Hydride Transfer Reactions: A  
Story of Selectivity Control**      P14  
Qiang Liu**12:15**      **Group Photo****12:30**      **Lunch – Sage Bistro**

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**AFTERNOON SESSION I***Chair: Huaping Xu*

**14:00**      **PolyPendantAmines – Hydroaminoalkylation and ROMP for the Assembly of Functional Polymeric Materials**      P16  
Laurel Schafer

**14:25**      **Hierarchical Structured Carbon Materials for Flexible and Wearable Electronics**      P18  
Yingying Zhang

**14:50**      **Folding and Unfolding Mechanisms of Iron Sulfur Proteins Revealed by Single Molecule Force Spectroscopy**      P20  
Hongbin Li

**15:15**      **The Frame Guided Assembly**      P22  
Dongsheng Liu

**15:40**      **Coffee Break**

**AFTERNOON SESSION II***Chair: Michael O. Wolf*

**16:00**      **Inorganic Radiopharmaceutical Chemistry**      P24  
Chris Orvig

**16:25**      **Ligand Effects on the Structures and Properties of Gold Nanoclusters**      P26  
Quanming Wang

**16:50**      **Delineating Mechanistic Complexity After the Turnover-Limiting Step: The Secret Lives of Cu(I)-Acetylides**      P28  
Jason Hein

**17:15**      **Closing Remarks**

**18:00**      **Dinner**

## **ABSTRACTS OF LECTURES**

{in the order of presentation}

# Factoids about Tactoids: New Materials from Cellulose Nanocrystals

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Cellulose nanocrystals (CNCs) are obtained by treating biomass with sulfuric acid. CNCs are typically ~5-20 nm in diameter and ~100-500 nm in length, depending on the cellulose source and extraction method. When dispersed in water, CNCs form a chiral nematic lyotropic liquid crystal in water. In this fluid structure, CNCs organize into a layered arrangement where the orientation of the CNCs spiral into a helix. Upon drying, CNCs retain the chiral nematic order with a helical axis perpendicular to the substrate. When the pitch of the structure matches the wavelength of incident light, CNCs give coloured, iridescent films.

As CNCs are concentrated in water, they first assemble into liquid crystalline droplets called *tactoids*. These tactoids subsequently fuse and eventually merge to form a continuous, chiral nematic film of CNCs. We have undertaken a detailed study of tactoids in CNCs and have discovered their ability to selectively incorporate or reject nanoparticles, based on size. In this talk, I will discuss our fundamental investigations of tactoids, and how these studies can be used for applications, such as nanoparticle sorting and producing films with improved photonic properties.

**Keywords:** Liquid crystal, Cellulose nanocrystals, Tactoid, Materials chemistry

## References:

1. Wang, P.-X.; Hamad, W. Y.; MacLachlan, M. J. *Angew. Chem. Int. Ed.* **2018**, *130*, 3418-3423.
2. Tran, A.; Hamad, W. Y.; MacLachlan, M. J. *Langmuir* **2018**, *34*, 646-652.
3. Wang, P.-X.; Hamad, W. Y.; MacLachlan, M. J. *Angew. Chem. Int. Ed.* **2016**, *55*, 12460-12464.
4. Wang, P.-X.; Hamad, W. Y.; MacLachlan, M. J. *Nature Comm.* **2016**, *7*, 11515.
5. Shopsowitz, K.E.; Qi, H.; Hamad, W.Y.; MacLachlan, M.J. *Nature* **2010**, *468*, 422-425.

## Brief Curriculum Vitae



**Mark MacLachlan** received his B.Sc. degree in Honours Chemistry (1995) at UBC. He obtained his Ph.D. degree from the University of Toronto (1999), where he worked with Prof. Ian Manners and Prof. Geoffrey Ozin in the areas of inorganic polymers and materials. After completing a 2-year NSERC Postdoctoral Fellowship with Prof. Timothy Swager at M.I.T., he returned to UBC to begin as an Assistant Professor in 2001. He was promoted to Associate Professor in 2007 and to Full Professor in 2011.

Mark's research interests span supramolecular chemistry, macrocycle chemistry, nanomaterials, mesoporous materials, photonic structures, and biopolymers. He has received a Humboldt Fellowship for Experienced Researchers (2009-2010), an E. W. R. Steacie Memorial Fellowship (2012-2014), the Strem Award for Pure or Applied Inorganic Chemistry from the Canadian Society for Chemistry (CSC) (2013), the Rutherford Medal of the Royal Society of Canada (2013), a JSPS Invitational Fellowship for Research in Japan (2013), the Steacie Prize (2014), and the Award for Excellence in Materials Chemistry of the CSC (2015). He is a Fellow of the Royal Society of Canada, holds the Canada Research Chair in Supramolecular Materials, and is a Visiting Research Professor of Kanazawa University.

## Recent Publications:

1. Nguyen, T.-D.; Tang, D.; D'Acierno, F.; Michal, C. A.; MacLachlan, M. J. *Chem. Mater.* **2018**, 30, 1602-1609.
2. Terpstra, A. S.; Arnett, L. P.; Manning, A. P.; Michal, C. A.; Hamad, W. Y.; MacLachlan M. J. *Adv. Opt. Mater.* **2018**, 6, 1800163.
3. Beaulieu-Houle, G.; White, N. G.; MacLachlan, M. J. *Cryst. Growth Des.* **2018**, 18, 2210-2216.
4. Oechsle, A.-L.; Lewis, L.; Hamad, W. Y.; Hatzikiriakos, S. G.; MacLachlan, M. J. *Chem. Mater.* **2018**, 30, 376-385.
5. Carta, V.; Mehr, S. H. M.; MacLachlan, M. J. *Inorg. Chem.* **2018**, 57, 3243-3253.
6. Hiratani, T.; Hamad, W. Y.; MacLachlan, M. J. *Adv. Mater.* **2017**, 29, 1606083.

# Designed Synthesis and Chiroptical Response of Structurally Well-Defined Chiral Gold Clusters

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During the past decade much effort has been paid to investigate the chirality in metal clusters or nanoclusters because it is crucial in the design and development of new chiral catalysts and chiroptical devices. Recently, we synthesized a series of chiral gold clusters by using chiral amine ligands. The sigmoidally and reverse-sigmoidally arranged gold clusters give strong CD response with the anisotropy factors up to  $6 \times 10^{-3}$ . Theoretical calculations revealed that the strong CD responses are closely related to the gold cluster-dominated HOMO orbitals, thus correlating the CD responses with the geometrical arrangement of gold atoms. Furthermore, through monitoring the variation of CD, UV-vis and NMR spectra at elevated temperatures, we studied three structurally well-defined gold cluster compounds to probe how structural factors influence their stability upon heating. The biased chiroptical response is finally ascribed to a synergistic effect of distinct structural tunability of central diamino ligands, inter-cluster aurophilic interaction and steric hindrance. As a further step to develop new synthetic methods of chiral metal cluster compounds, we recently established a new synthetic strategy toward the construction of gold clusters with axial chirality based on organic transformations. Structure and CD response comprehension of these chiral metal clusters foresees deep research in understanding the origin of chirality in metal clusters and stimulates the advancement of designing novel chiroptical functional materials.

**Keywords:** Chiral metal clusters, Chiroptical response, Gold complexes

## References:

1. He, X.; Wang, Y.; Jiang, H.; Zhao, L. *J. Am. Chem. Soc.* **2016**, *138*, 5634.
2. Yuan, J.; Sun, T.; He, X.; An, K.; Zhu, J.; Zhao, L. *Nat. Commun.* **2016**, *7*, 11489.
3. Guo, P.; Yang, B.; Zhang, L.; Zhao, L. *Chem. Sci.* **2018**, *9*, 5614.
4. Xue, Y.; Yang, B.; Zhao, L. *unpublished results*.

## Brief Curriculum Vitae



**Liang Zhao** was born in June 1981, China. He firstly studied chemistry at the College of Chemistry and Molecular Engineering in Peking University and obtained his bachelor degree in 2002. After staying for another year as a research assistant at the State Key Laboratory for Structural Chemistry of Unstable and Stable Species also in Peking University, he enrolled in the Chemistry Department of the Chinese University of Hong Kong under the guidance of Prof. Thomas C. W. Mak (UBC alumni, 1957-1963) and graduated with a PhD degree in Chemistry in 2007. Subsequently, he joined Prof. Peter J. Stang's research group at University of Utah and completed two-year postdoctoral studies until September 2009. In November 2009, he joined the faculty of Chemistry Department in Tsinghua University as an Associate Professor. His awards include Chinese Chemical Society Prize for Young Scientists (2013), National Science Funds for Excellent Young Scholars (2015), and Young Changjiang Scholars (2016). His research interest is focused on the interdisciplinary area of supramolecular and organometallic chemistry, especially the controllable synthesis and reactivity studies of polynuclear organometallic clusters.

### Representative Publications:

1. Guo, P.; Yang, B.; Zhang, L.; Zhao, L.\* *Chem. Sci.* **2018**, 9, 5614-5622.
2. He, X.; Xue, Y.; Li, C.-C.; Wang, Y.; Jiang, H.; Zhao, L.\* *Chem. Sci.* **2018**, 9, 1481-1487.
3. Zhang, Q.-Y.; He, X.; Zhao, L.\* *Chem. Sci.* **2017**, 8, 5662-5668.
4. Yuan, J.; Sun, T.; He, X.; An, K.; Zhu, J.\*; Zhao, L.\* *Nat. Commun.* **2016**, 7, 11489.
5. He, X.; Wang, Y.; Jiang, H.; Zhao, L.\* *J. Am. Chem. Soc.* **2016**, 138, 5634-5643.
6. He, X.; Liu, H.-X.; Zhao, L.\* *Chem. Commun.* **2016**, 52, 5682-5685.
7. He, X.; Wang, Y.; Gao, C.-Y.; Jiang, H.; Zhao, L.\* *Chem. Sci.* **2015**, 6, 654-658.
8. Liu, H.-X.; He, X.; Zhao, L.\* *Chem. Commun.* **2014**, 50, 971-974.
9. Gao, C.-Y.; Zhao, L.\*; Wang, M.-X.\* *J. Am. Chem. Soc.* **2012**, 134, 824-827.
10. Gao, C.-Y.; Zhao, L.\*; Wang, M.-X.\* *J. Am. Chem. Soc.* **2011**, 133, 8448-8451.

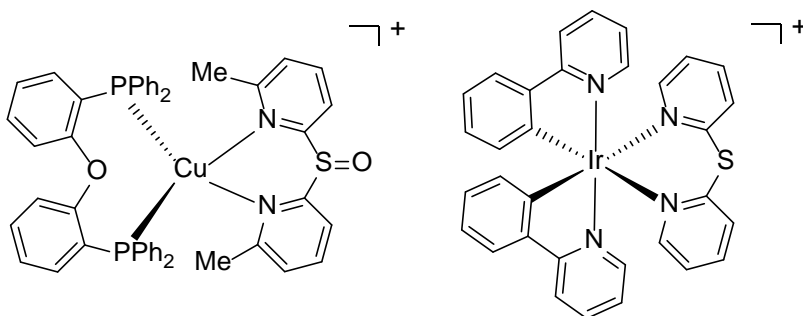


# Photophysics and Photochemistry of Sulfur-Bridged Chromophores

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Sulfur-based functional groups (sulfides, sulfoxides and sulfones) provide a convenient, tunable approach to varying the electronic behaviour of conjugated compounds, while maintaining a consistent steric environment. Sulfoxide and sulfone ligands also present dual binding sites (via oxygen and sulfur atoms) resulting in a diversity of binding modes in polydentate ligands for metals. We have found that symmetrically substituted conjugated ligands bridged by sulfur groups can have low-lying, emissive intramolecular charge transfer states which can also influence electronic properties of complexes bearing these as ligands, and allow applications in devices such as light-emitting diodes. A series of new sulfur-containing ligands, and Cu, Ir and Ru complexes containing these ligands, will be described. The photophysical behaviour of these complexes will be discussed, focusing on the electronic tunability of this ligand set, and the resulting photophysical and photochemical changes exhibited by the complexes.



**Keywords:** Photophysics, Coordination complexes, Photochemistry, Conjugated compounds

## Brief Curriculum Vitae



**Michael Wolf**, obtained his bachelor degree in Biochemistry from Dalhousie University in 1989 and PhD degree in Chemistry from the Massachusetts Institute of Technology (with Prof. Mark S. Wrighton) in 1994. After his training as NSERC Postdoctoral Fellow at the Department of Chemistry, University of Texas at Austin (with Prof. Marye A. Fox, 1994-1995), he joined the Department of Chemistry at the University of British Columbia as an Assistant Professor in 1995. Currently he is a full Professor and Head of Chemistry. His awards include the CSC Rio Tinto Alcan Award, CSC Award for Pure or Applied Inorganic Chemistry, and UBC Killam

Research Prize. His research interests include Conjugated materials with optoelectronic applications – synthesis and photophysics of new conjugated oligomers and polymers; Applications of conjugated materials in biological imaging, photopatterning, solar cells and light-emitting devices; Electrocatalytic carbon dioxide reduction with homogeneous catalysts; Nanostructured catalysts for methane oxidation; and Synthesis and study of new photochromic compounds in solution and in the solid state.

### Selected Publications

1. Brown, C. M.; Kitt, M. J.; Xu, Z.; Hean, D.; Ezhova, M. B.; Wolf, M. O. *Inorg. Chem.* **2017**, 56, 15110-15118.
2. Cao, Y.; Wang, X. Z.; Shi, X. L.; Clee, S. M.; McGeer, P. L.; Wolf, M. O.; Orvig, C. *Angew. Chem. Int. Ed.* **2017**, 56, 15603-15606.
3. Christensen, P. R.; Wolf, M. O. *Adv. Funct. Mater.* **2016**, 26, 8471-8477.
4. Cao, Y.; Wolf, M. O.; Patrick, B. O. *Inorg. Chem.* **2016**, 55, 8985-8993.
5. Cruz, C. D.; Christensen, P. R.; Chronister, E. L.; Casanova, C.; Wolf, M. O.; Bardeen, C. J. *J. Am. Chem. Soc.* **2015**, 137, 12552-12564.
6. Cao, Y.; Wolf, M. O.; Patrick, B. O. *J. Am. Chem. Soc.* **2015**, 137, 4888-4891.
7. Christensen, P. R.; Patrick, B. O.; Caron, É.; Wolf, M. O. *Angew. Chem. Int. Ed.* **2013**, 52, 12946-12950.

# Dynamic Chemistry of Selenium-containing Polymers

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Dynamic covalent bonds are extensively employed in dynamic combinatorial chemistry and self-healing materials. We found that diselenide bonds are dynamic covalent bonds and diselenide metathesis can be induced by visible light without additives. The metathesis reaction was determined to undergo a radical mechanism. This dynamic chemistry can also be used in polymer systems as well as in self-healing materials. The diselenide bond containing elastomer could be remotely healed by a visible light laser. In further research, via metathesis at water/oil interfaces, the equilibrium of diselenide metathesis could be controlled and asymmetric diselenide product could be stabilized. Selenium-nitrogen bond (Se-N) was used as intermediates in some reactions, while after studied the properties of the bond itself, we found that Se-N bond, between the Se atom of a phenylselenyl halogen species and the N atom of a pyridine derivative, is also a dynamic covalent bonds. It can be reversibly and rapidly formed or cleaved under acidic or basic conditions, respectively. The work in our lab introduced selenium into dynamic chemistry, opened a new research field of selenium and developed new self-healing materials and shape-memory materials.

**Keywords:** Dynamic covalent bonds, Selenium, Responsive polymer

## References:

1. Xu, H.; Cao, W.; Zhang, X. *Acc. Chem. Res.* **2013**, *46*, 1647.
2. Yi, Y.; Xu, H.; Wang, L.; Cao, W.; Zhang, X. *Chem. Eur. J.*, **2013**, *19*, 9506.
3. Ji, S.; Cao, W.; Yu, Y.; Xu, H. *Angew. Chem., Int. Ed.* **2014**, *53*, 6781.
4. Ji, S.; Cao, W.; Yu, Y.; Xu, H. *Adv. Mater.*, **2015**, *27*, 7740.
5. Cao, W.; Wang, L.; Xu, H. *Nano Today*, **2015**, *10*, 717.
6. Huang, X.; Fang, R.; Wang, D.; Wang, J.; Xu, H.; Wang, Y.; Zhang, X. *Small*, **2015**, *11*, 1537.
7. Ji, S.; Xia, J.; Xu, H. *ACS Macro Lett.*, **2016**, *5*, 78.
8. Xia, J.; Ji, S.; Xu, H. *Polym. Chem.*, **2016**, *7*, 6708.
9. Ji, S.; Fan, F.; Sun, C.; Yu, Y.; Xu, H. *ACS Appl. Mater. Interfaces*, **2017**, *9*, 33169.
10. Ji, S.; El Mard, H.; Smet, M.; Dehaen, W.; Xu, H. *Sci. China Chem.*, **2017**, *60*, 1191.

## Brief Curriculum Vitae



**Huaping Xu**, born in 1978, received his Bachelor degree in 2001 and Ph. D. degree in 2006 in Jilin University, China, under the supervision of Prof. Xi Zhang. During 2004-2005, he worked as an exchange student in University of Leuven, Belgium. In 2006, he joined Prof. David N. Reinhoudt and Prof. Jurriaan Huskens's group at University of Twente, the Netherlands as a post-doc. Since July 2008, he has worked at Department of Chemistry, Tsinghua University, China. He was promoted to full professor in 2014. In 2014, he received the Natural Science Fund for Outstanding Young Scholars from NSFC. In 2017, he was enrolled in Leading Talent of National High-level personnel of special support program ("people plan"). He received Nano Research Young Innovator Awards in NanoBiotech 2018. He has served for Associate Editor of *ACS Biomaterials Science & Engineering* since January 2017. His current research is focused on selenium/tellurium-containing polymers.

### Representative Publications:

1. Li, F.; Li, T.; Sun, C.; Xia, J.; Jiao, Y.; Xu, H. *Angew. Chem. Int. Ed.*, **2017**, 56, 9910.
2. Ji, S.; Cao, W.; Yu, Y. and Xu, H. *Adv. Mater.*, **2015**, 27, 7740.
3. Xu, H.; Cao, W.; Zhang, X. *Acc. Chem. Res.*, **2013**, 46, 1647.
4. Ji, S.; Cao, W.; Yu, Y.; Xu, H. *Angew. Chem. Int. Ed.*, **2014**, 53, 6781.
5. Cao, W.; Gu, Y.; Meineck, M.; Li, T.; Xu, H. *J. Am. Chem. Soc.*, **2014**, 136, 5132.
6. Cao, W.; Zhang, X.; Miao, X.; Yang, Z.; Xu, H. *Angew. Chem. Int. Ed.*, **2013**, 52, 6233.
7. Ma, N.; Li, Y.; Xu, H.; Wang, Z.; Zhang, X. *J. Am. Chem. Soc.*, **2010**, 132, 442.

# Ordered Multiblock Nanofibers from Organic Electronic Materials

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Techniques for the assembly of hierarchical nanostructures from soft matter have opened the door to many new applications of nanotechnology. Methods such as crystallization-driven self-assembly, living supramolecular polymerization, and hierarchical solution self-assembly have leveraged low-cost solution processing to address scalability challenges, while the complexity of materials prepared in these ways continues to improve. Here we present methods for the preparation of fiber-like nanomaterials which mimic the multilayer structure of organic electronic devices on individual polymer chains. By combining Cu(0) reversible-deactivation radical polymerization (RDRP) and ring-opening metathesis polymerization (ROMP), multiblock bottlebrush copolymers are synthesized from ordered sequences of organic semiconductors. Narrowly dispersed fibers are prepared from materials commonly used as the hole transport, electron transport, and host materials in organic electronics, with molecular weights exceeding  $2 \times 10^6$  Da and dispersities as low as 1.12. Diblock nanofibers are then synthesized from pairs of semiconducting building blocks, giving nanostructures analogous to p-n junctions that exhibit the reversible electrochemistry of their individual parts. Finally, this strategy is used to construct nanofibers with the structure of phosphorescent organic light-emitting diodes (OLEDs) on single macromolecules, such that the photophysical properties of each component of an OLED can be independently observed. This work opens the door to research on nanoscale wires and junctions from arbitrary organic semiconductors regardless of their crystallinity or solvophilicity, providing methods for the incorporation of diverse optoelectronic materials into hierarchical nanofibers.

**Keywords:** Block copolymers, organic electronics, soft-matter nanomaterials.

## References:

1. Tonge, C.M.; Sauv , E.R.; Cheng, S.; Howard, T. A.; Hudson, Z.M. **2018**, *submitted*.
2. Tonge, C.M.; Sauv , E.R.; Paisley, N.R.; Heyes, J. E.; Hudson, Z.M. *Polym. Chem.* **2018**, *9*, 3359-3367.
3. Sauv , E.R.; Tonge, C.M.; Paisley, N.R.; Cheng, S.; Hudson, Z.M. *Polym. Chem.* **2018**, *9*, 1397-1403.

## Brief Curriculum Vitae



**Zachary M. Hudson** is an Assistant Professor and Canada Research Chair in Sustainable Chemistry at the University of British Columbia. Zac was born in Ottawa in 1986, and completed his B.Sc. at Queen's University in Kingston, Ontario. He remained at Queen's to pursue a Ph.D. in Inorganic Chemistry under the supervision of Prof. Suning Wang, focusing on the development of luminescent materials for organic electronics. During his Ph.D. he also held graduate fellowships at Jilin University in China as well as Nagoya University in Japan. He then moved to the

University of Bristol as a Marie Curie Postdoctoral Fellow with Prof. Ian Manners, followed by a second Postdoctoral Fellowship at the California Nanosystems Institute at the University of California, Santa Barbara with Prof. Craig Hawker. He currently leads a research program examining a variety of questions in synthetic materials chemistry, ranging from the development of solutions for energy-efficient displays and light sources to the self-assembly of electronic materials on the nanoscale.

### Representative Publications:

1. Qiu, H.; Hudson, Z.M.; Winnik, M.A.; Manners, I. *Science* **2015**, *347*, 1329-1332.
2. Hudson, Z.M.; Boott, C.E.; Robinson, M.E; Rugar, P.A.; Winnik, M.A.; Manners, I. *Nature Chemistry* **2014**, *6*, 893-898.
3. Hudson, Z.M.; Lunn, D.J.; Winnik, M.A.; Manners, I. *Nature Commun.* **2014**, *5*:3372.
4. Hudson, Z.M.; Sun, C.; Helander, M.G.; Chang, Y.-L.; Lu, Z.-H.; Wang, S. *J. Am. Chem. Soc.* **2012**, *134*, 13930-13933.

# Cobalt-Catalyzed Hydride Transfer Reactions: A Story of Selectivity Control

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Hydride transfer reactions constitute a broad class of chemical reactions involving transfer processes of hydrogen in the form of hydride. Such reactions are commonly catalytic and involve a metal hydride species as an indispensable catalytically active intermediate. These transformations play essential roles in both organic synthesis and chemical industry, providing convenient access to a variety of valuable chemical products. Most hydride transfer reactions rely on precious metal catalysts. However, use of these metals is limited by their high cost, low abundance, and toxicity. In contrast, application of first-row transition metals as catalysts is much more sustainable and addresses the disadvantages of precious metal catalysis. For example, the reserve of elemental cobalt is over 1000 times larger than the total content of platinum-group metals in the Earth's crust, highlighting the relative abundance of first-row transition metals. In addition, these earth-abundant metals feature much better biological compatibility and lower toxicity. As a result, substitution of precious metal catalysts in hydride transfer reactions with economical and ecologically friendly earth-abundant metal catalysts is highly desirable in terms of sustainability. In addition, the multiple spin states, variable coordination geometries, and inimitable electronic properties of non-precious metals enable unprecedented reactivity, distinct mechanistic pathways, and unique substrate scope. Therefore, the development of non-noble metal catalysis offers an opportunity to develop hydride transfer reactions in a new chemical space. Since the discovery of hydroformylation reactions in 1940s, cobalt has been established as an efficient catalyst for a variety of hydride transfer reactions. The utility of cobalt catalysis has been markedly expanded in the past decade along with the development of various well-defined cobalt complexes as effective homogenous catalysts for hydride transfer processes. In this respect, we developed a novel kind of pincer cobalt catalysts in high spin state, which revealed unique advantages for the precise selectivity control in catalytic hydride transfer reactions.

**Keywords:** Cobalt Catalysis, Hydride Transfer Reactions, Selectivity Control

## References:

1. Filonenko, G. A.; Putten, R. van.; Hensen, E. J. M.; Pidko, E. A. *Chem. Soc. Rev.* **2018**, *47*, 1459.
2. Chirik, P. J. *Acc. Chem. Res.* **2015**, *48*, 1687.
3. Corma, A.; Navas, J.; Sabater, M. J. *Chem. Rev.* **2018**, *118*, 1410.

## Brief Curriculum Vitae



**Qiang Liu**, was born in China in 1984. He obtained his bachelor degree in Chemistry from Wuhan University in 2007 and PhD degree in Organic Chemistry from Wuhan University (with Prof. Aiwen Lei) in 2012. Then he moved to Leibniz Institute for Catalysis in Germany as a Humboldt postdoctoral fellow (with Prof. Matthias Beller). In 2015, he was selected by the “1000 young talent plan” and joined the faculty of Chemistry Department at Tsinghua University as an associate professor. He received Thieme Chemistry Journals Award in 2017. Currently, he is interested in the development

of non-noble metal catalysis, energy molecules activation, and sustainable energy conversion system.

### Representative Publications:

1. Liu, X.; Zhang, W.; Wang, Y.; Zhang, Z.-X.; Jiao, L.; Liu, Q. *J. Am. Chem. Soc.* **2018**, *140*, 6873.
2. Qi, X.; Liu, X.; Qu, L.-B.; Liu, Q.; Lan, Y. *J. Catal.* **2018**, *362*, 25.
3. Fu, S.; Shao, Z.; Wang, Y.; Liu, Q. *J. Am. Chem. Soc.* **2017**, *139*, 11941.
4. Shao, Z.; Fu, S.; Wei, M.; Zhou, S.; Liu, Q. *Angew. Chem. Int. Ed.* **2016**, *55*, 14653.
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# PolyPendantAmines – Hydroaminoalkylation and ROMP for the Assembly of Functional Polymeric Materials

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N,O-Chelated complexes of early transition metals offer unique reactivity in atom economic hydrofunctionalization transformations, such as hydroaminoalkylation.[1] The efficient synthesis of amine functionalized cyclic alkenes by hydroaminoalkylation has enabled the facile assembly of tunable, amine-containing polymeric materials by ROMP.[2] The resulting polypendantamines have dynamic hydrogen bonding interactions that offer flexible intra- and intermolecular interactions. The incorporation of amines with variable hydrogen bonding capabilities has resulted in materials with dramatically tunable viscoelastic properties, such that the same catalyst system can access liquid, gel or solid rheological behaviors using the same number of repeat units.[3] Furthermore, self-healing and remarkable adhesive properties have been realized. Advances in catalyst development that has enabled the multi-gram scale synthesis of these responsive materials will be presented. Mechanistic insights into Grubbs catalyzed ROMP with unprotected amine containing monomers, including the preparation, characterization and analysis of block-copolymers, will also be discussed. Finally, the breadth of physical properties that can be accessed with these functional materials will be featured.

**Keywords:** Hydrofunctionalization, Hydroaminoalkylation, ROMP, Polymers, Functional Materials

## References:

1. Chong, E.; Garcia, P.; Schafer, L. L., *Synthesis*, **2014**, *46*, 2884-2896,
2. Perry, M. R.; Ebrahimi, T.; Morgan, E.; Edwards, P. M.; Hatzikiriakos, S. G.; Schafer, L. L. *Macromolecules*, **2016**, *49*, 4423-4430.
3. Gilmour, D. J.; Tomkovic. T.; Perry, M. R.; Hsiang, E.; Hatzikiriakos, S. G.; Schafer, L. L. Manuscript Submitted.

## Brief Curriculum Vitae



**Laurel Schafer**, received her BSc from the University of Guelph in 1993, and her PhD from the University of Victoria in 1999 under the supervision of Prof. D. J. Berg. She then went on to the University of California-Berkeley to complete an NSERC post-doctoral fellowship with Prof. T. D. Tilley. In 2001, she joined the University of British Columbia in Vancouver and has risen to the rank of full Professor and currently holds a Canada Research Chair in Catalyst Development (Tier II). The Schafer group has developed new families of

N,O-chelated early transition metal complexes for atom-economic catalysis to prepare amines, heterocycles, enynes and biodegradable polymers. In particular, the group specializes in organometallic catalysis for organic synthesis including reaction kinetics and mechanistic investigations. These catalysts can be used in tandem sequential reactions for the efficient synthesis of biologically active small molecules and functionalized, responsive materials.

### Representative Publications:

1. Lui, E. K. J.; Brandt, J. W.; Schafer, L. L. *J. Am. Chem. Soc.*, **2018**, *140*, 4973-4976.
2. DiPucchio, R. C.; Rosca, S.-C.; Schafer, L. L. *Angew. Chem., Int. Ed.*, **2018**, *57*, 3469-3472.
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# Hierarchical Structured Carbon Materials for Flexible and Wearable Electronics

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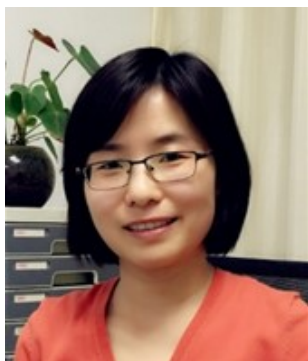
The development of flexible electronics and equipment attracts significant interests in recent years. Carbon materials are one kind of ideal materials for flexible electronics. It is of great importance to explore low cost and scalable preparation approaches for high performance flexible carbon materials-based wearable electronics. Herein, we use carbon materials, including carbon nanotubes, graphene, and natural mass derived carbon (such as silk, cellulose) as the key materials and develop a series of flexible wearable sensors, wires and energy devices [1-5]. The hierarchical structures of the carbon materials plays important roles in achieving flexible devices with desired performance. We further demonstrated their applications and show their great potentials for applications in wearable electronics and smart textiles. Our strategy provides new approaches for the low-cost and high performance production of carbon-based flexible and wearable electronic materials, shedding light on their practical applications in next-generation electronics.

**Keywords:** Carbon Nanomaterials, Silk Fabric, Strain Sensor, Wearable Electronics, Smart Textiles

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## Brief Curriculum Vitae



**Yingying Zhang** received her her Ph.D. degree in physical chemistry from Peking University in 2007. From Jun. 2008 to Jun. 2011, she worked in Los Alamos National Laboratory (USA) as a postdoctoral research associate. Then, she joined Tsinghua University as an associate professor in July of 2011. Her research focuses on the synthesis and basic understanding of carbon nanotubes (CNTs), graphene, silk, and their hybrid materials, toward developing high performance flexible and wearable electronics and smart systems. She has authored

more than 80 journal papers, including *Nat Nanotechnol*, *Nat Commun*, *Adv Mater*, *JACS*, *Nano Lett*, *ACS Nano*, *Adv Funct Mater* etc, with more than 1800 citations. Besides, she has authored 2 book chapters, and 22 patents (8 awarded). She has been supported/ awarded by National Science Fund for Excellent Young Scholar (2014), Young Cutting-Edge Nanochemistry Researcher Award (2014), National Program for Support of Top-notch Young Professionals (2016), and young scholars of Yangtze River scholar professor program (2017).

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# Folding and Unfolding Mechanisms of Iron Sulfur Proteins Revealed by Single Molecule Force Spectroscopy

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Metal ions play important roles in biology. In metalloproteins, metal centers serve as active sites, as well as important structural elements to facilitate protein folding and assembly. However, it is challenging to investigate the unfolding-folding of metalloproteins due to the loss or decomposition of the metal center. Here, we combine single molecule force spectroscopy and protein engineering to investigate the unfolding-refolding mechanism of small iron sulfur proteins rubredoxin and ferredoxin. Our results revealed that the unfolding of both proteins are characterized by the initial partial unfolding of the protein followed by the rupture of the iron sulfur center and complete unraveling of the protein. However, differences in the iron chelation motif in rubredoxin and ferredoxin gave rise to distinct rupture patterns of the iron sulfur center. After complete unfolding, rubredoxin and ferredoxin were observed to refold to its holo-native form with the fully reconstituted iron sulfur center. Moreover, folding of the apo- rubredoxin was observed during the folding of rubredoxin, while apo-ferredoxin was not observed to form, revealing different roles and importance of the iron sulfur center to the holo-proteins. Our results open new avenues towards investigating the folding mechanism of metalloproteins at an unprecedented resolution.

**Keywords:** single molecule, metalloproteins, force spectroscopy, protein folding

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## Brief Curriculum Vitae



**Hongbin Li**, was born in China in 1970. He obtained his bachelor degree in Polymer Engineering from Tianjin University in 1993 and PhD degree in Polymer Chemistry and Physics from Jilin University (with Profs. Jiacong Shen, Xi Zhang and Hermann Gaub) in 1998. During his PhD study, he was jointly trained in University of Munich, Germany. After his postdoctoral training in Mayo Medical Center in Rochester, Minnesota, USA (with Prof. Julio Fernandez, 1999-2002), he worked as an Associate Research Scientist in Columbia University, USA. In 2004,

he joined the Department of Chemistry in the University of British Columbia, Canada. Currently he is a full Professor in Chemistry. His awards include the Charles McDowell Award for Excellence in Research, Canada Research Chair in Molecular Nanoscience and Protein Engineering, NSERC Discovery Accelerator Supplement Award, Michael Smith Foundation for Health Research Career Investigator Award, Peter Wall Institute Early Career Award, JILA Distinguished Visitor Fellow and Changjiang Scholar. His research interests include protein mechanics and engineering at the single molecule level, protein-based biomaterials, as well as protein folding and unfolding dynamics.

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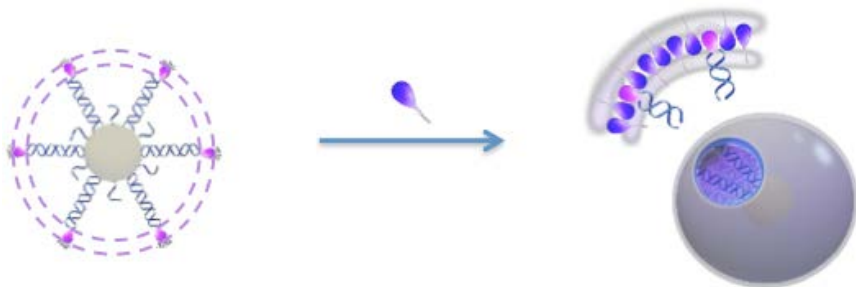
# The Frame Guided Assembly

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How to precisely control the shape and size of final assemblies, especially using same amphiphilic molecules and under the same environmental conditions, is always a challenge in molecular assembly. Inspired by the cytoskeletal/membrane protein/lipid bilayer system that determines the shape of eukaryotic cells, we proposed and 'the Frame Guided Assembly' (FGA) strategy to prepare heterovesicles with programmed geometry and dimensions. This method offers greater control over self-assembly: with same molecular system, the size of final assemblies could be tuned at 1 nm level and their shape could vary from spherical to cubic, and even given sized two dimensional sheets. Most importantly, the principle of the FGA could be applied to various materials such as block copolymers, small molecules including surfactants and lipids, which is a general rule in self-assembly.



Scheme 1. Schematic illustration of the Frame Guided Assembly

**Keywords:** Assembly, Shape control, size control

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## Brief Curriculum Vitae



**Dongsheng Liu** learned polymer sciences in University of Science and Technology of China and graduated with a B.S. degree in 1993. He then worked as a research associate in the Institute of Chemistry, CAS for six years and earned his Master degree on polymer chemistry in 1999. From 1999 to 2002, he finished his Ph.D study on the self-templated DNA circularization in the Hong Kong Polytechnic University under the supervision of Professor Albert S. C. Chan. In 2003, he joined the Chemistry Department of Cambridge

University as a postdoc research associate, worked on DNA nanotechnology with Professor Shankar Balasubramanian. In 2005, he joined the National Centre for NanoScience and Technology, China as a principle investigator and in June 2009, he moved to the Department of Chemistry, Tsinghua University as a full professor. He was awarded the 1st “CCS-RSC Young Chemist Award” in 2008, the 7th CCS-BASF Youth Innovation Prize in 2014. Dongsheng was invited as FRSC in 2011 and became “Changjiang” Chair Professor in 2015. His research mainly focuses on DNA molecular machines and DNA based smart materials.

### Representative Publications:

1. Shao, Y.; Jia, H.; Cao, T.; Liu, D\*. *Acc. Chem. Res.*, **2017**, *50*, 659–668.
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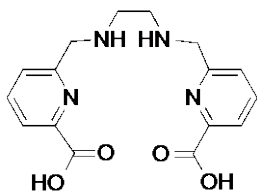


# Inorganic Radiopharmaceutical Chemistry

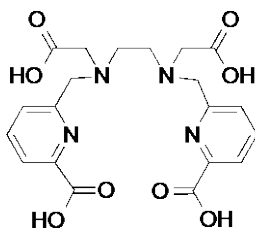
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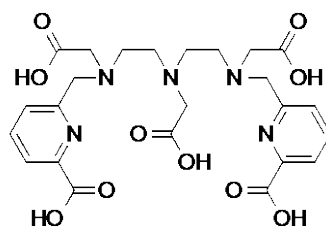
Significant research effort has investigated new bifunctional chelate alternatives to the  $N_3$  and  $N_4$  aminocarboxylate macrocycles NOTA or DOTA, respectively, for the isotopes  $^{66,67,68}\text{Ga}$ ; however, NOTA and DOTA have become the “gold standard”. We report our findings concerning the linear  $N_4O_2$  chelate  $\text{H}_2\text{dedpa}$  and the linear  $N_4O_4$  chelate  $\text{H}_4\text{octapa}$  plus larger analogues for application with a wide variety of radiometal ions useful for imaging, diagnosis and therapy. Concentration dependent labelling after 10 minutes reaction at RT of these ligands with many radiometal ions showed quantitative conversion to the desired products with ligand concentrations as low as  $10^{-7}$  M. With  $^{68}\text{Ga}$  and  $[\text{dedpa}]^{2-}$ , specific activities as high as  $9.8 \text{ mCi nmol}^{-1}$  were obtained without purification. Most notably, in a 2h competition experiment against human *apo*-transferrin,  $^{67}\text{Ga}(\text{dedpa})^+$  showed no decomposition. In a direct competition for chelation of  $^{67}\text{Ga}$  with equal concentrations of both NOTA and  $\text{H}_2\text{dedpa}$ , over 96% of the gallium isotope was coordinated to  $\text{dedpa}^{2-}$ . Bifunctional analogues of  $\text{H}_2\text{dedpa}$  and  $\text{H}_4\text{octapa}$  all label various  $M^{3+}$  at RT within 10 minutes. The stabilities of these building blocks and their modular family of easily accessible ligands, such as  $\text{H}_5\text{decapa}$ , are comparable to, or higher than, that of DOTA; the “pa” family of ligands, and a new family using 8-hydroxyquinoline arms are under intense current investigation, as are the biodistribution profiles of these platform chelate candidates with a variety of radiometal ions (e.g.  $^{64}\text{Cu}^{2+}$ ,  $^{111}\text{In}^{3+}$ ,  $^{89}\text{Zr}^{4+}$ ,  $^{86,90}\text{Y}^{3+}$ ,  $^{177}\text{Lu}^{3+}$ ,  $^{225}\text{Ac}^{3+}$  etc.).



**$\text{H}_2\text{dedpa}$**



**$\text{H}_4\text{octapa}$**



**$\text{H}_5\text{decapa}$**

## Brief Curriculum Vitae



**Chris Orvig** obtained his First Class Honors BSc in Chemistry at McGill in 1976. He then studied at the Massachusetts Institute of Technology as an NSERC of Canada Postgraduate Scholar (PGS), obtaining his PhD in 1981. After two years at the University of California, Berkeley as an NSERC Postdoctoral Fellow (PDF) with Prof. K. N. Raymond, and an additional year at McMaster University with Prof. C. J. L. Lock, he joined the Chemistry Department at UBC in 1984 as an NSERC University Research Fellow and he was named Professor of Chemistry in 1995. He was acting Head of Chemistry in 2000-2001 and Associate Head of Chemistry in 2010-11. He edited the

September 1999 *Chemical Reviews* special issue on Medicinal Inorganic Chemistry, the first comprehensive treatise in this field, and he was invited by *Science* to review the field in 2003. He serves on many editorial and institutional boards (chairing that for *Dalton Transactions* 2008-2011), and was the inorganic chemistry editor of the *Canadian Journal of Chemistry* for ten years. He chaired the 31st International Conference on Coordination Chemistry (ICCC) at UBC in 1996, the 2004 Metals in Medicine Gordon Research Conference, and the 15<sup>th</sup> International Conference on Biological Inorganic Chemistry (ICBIC) at UBC in 2011. He is now the Executive Secretary for the ICCC.

Orvig's research has been recognized by receipt of an Alexander von Humboldt Research Prize (Germany), a Japan Society for the Promotion of Science (JSPS) Invitation Fellowship, and UBC Killam Awards for research and teaching. In 2009, he received both the Rio Tinto Alcan Award, for inorganic or electrochemistry, from the Canadian Society for Chemistry, and the Bioinorganic Chemistry Award from the Royal Society of Chemistry. He was elected Fellow of the Royal Society of Canada in 2010; he was Davison Lecturer at MIT in 2011 and G. Ronald Brown Lecturer at McGill in 2014. He won a Canada Council for the Arts Killam Research Fellowship for 2011-2013, and UBC's highest research honour, the Jacob Biely Research Prize, in 2013. The Alexander von Humboldt Foundation named him Humboldt Ambassador Scientist for 2015-2021.

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# Ligand Effects on the Structures and Properties of Gold Nanoclusters

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Ligand-protected gold nanoclusters have been attracting extensive attention, because of their tailorable geometric and electronic structures. They are promising molecular materials for potential applications in catalysis, biosensing, luminescence and molecular electronics, etc.<sup>1</sup> Their precise compositions and well-defined sizes are advantageous to understand the structure-property relationships of metal nanoclusters. Beyond the conventional thiolate and phosphine ligands, alkynyl ligands have emerged as promising agents in protecting gold nanoclusters.<sup>2</sup> As the ligand space has been broadened, new cluster compositions, structures and interfaces can be expected. We developed a “direct reduction” method to prepare a series of alkynyl-protected gold nanoclusters, managed to achieve their total structure determination. Structure control of these gold nanoclusters can be realized using various ligands. The stability and optical properties of these nanoclusters will be discussed based on coordination preference and electronic structural analysis. The influence of ligands on the luminescence and catalytic performance of gold nanoclusters will be presented. The success in these systems demonstrates the important role of alkynyl ligands in the formation of gold nanocluster, which dictates the properties of the clusters.<sup>3</sup>

**Keywords:** Gold nanoclusters, Structure control, Ligand effects

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## Brief Curriculum Vitae



**Quan-Ming Wang**, was born in China in 1967. He obtained his bachelor and Master degrees in Physical Chemistry from Xiamen University in 1989 and 1993, respectively. He obtained PhD degree in Chemistry from The Chinese University of Hong Kong (with Prof. Thoma C. W. Mak) in 2001. He did his postdoctoral work in CUHK (with Prof. Mak, 2001-2002), Rochester University (with Prof. Richard Eisenberg, 2002-2004) and UC Riverside (with Prof. Pingyun Feng, 2004-2005). In 2005, he joined the Department of Chemistry in Xiamen University, and he moved to Tsinghua University in 2015. Currently he is a full

Professor in Department of Chemistry of Tsinghua University. His research interests include rational synthesis of coinage metal clusters, luminescent cluster compounds and nanocluster-based catalysis.

### Representative Publications:

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# Delineating Mechanistic Complexity After the Turnover-Limiting Step: The Secret Lives of Cu(I)-Acetylides

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$\sigma$ -Copper acetylides represent a very versatile class of reactive intermediates, common to a plethora of Cu(I)-catalyzed transformation of terminal alkynes. A particularly attractive feature of these intermediates is their ability to deliver target products with exquisite chemo- and regioselectivity, despite synthetic conditions, which on their surface, should allow for competing reaction pathways to persist. Controlling and explaining the superior selectivity of these processes requires a detailed understanding of all ancillary equilibria within a complex reaction network. Ultimately, a fundamental understanding of the ensemble of associated equilibria present within these synthetic transformations is critical for the development of practical applications.

In order to efficiently study such complex reaction networks, my group has developed an approach that leverages a combination of in-situ reaction monitoring techniques, including ReactIR, reaction calorimetry and automated reaction sampling. This tandem application of process analytical technology allows us to rapidly deconvolute convoluted pathways and competing reactions, reducing complex kinetic analysis to simple pattern recognition. This new mode of reaction analysis is exceptionally well suited to study multicomponent reactions with a variety of competing processes. Application of these techniques to delineate the underlying catalytic networks involving  $\sigma$ -copper acetylides will be discussed.

**Keywords:** Reaction Progress Kinetic Analysis, Catalysis, Reaction Mechanism

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## Brief Curriculum Vitae



**Jason Hein** received his B.Sc. in Biochemistry in 2000 and Ph.D. in asymmetric reaction methodology in 2005 from the University of Manitoba (NSERC PGS-A/B, Prof. Philip G. Hultin). In 2006, he became an NSERC postdoctoral research fellow with Prof. K. Barry Sharpless and Prof. Valery V. Fokin at the Scripps Research Institute in La Jolla, CA. In 2010, he became a senior research associate with Prof. Donna G. Blackmond at the Scripps Research Institute. He began his independent career at the University of California,

Merced in 2011, employing in-situ kinetic reaction analysis as a means to rapidly profile and study complex networks of reactions. In 2015, he moved to the University of British Columbia to continue the development of automated reaction analytical technology to serve mechanistic organic chemistry. Current studies are aimed at solving a diverse set of problems, including understanding mechanisms of catalyst induction and deactivation, as well as developing techniques to resolve racemic mixtures using coupled preferential crystallization.

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## NOTES