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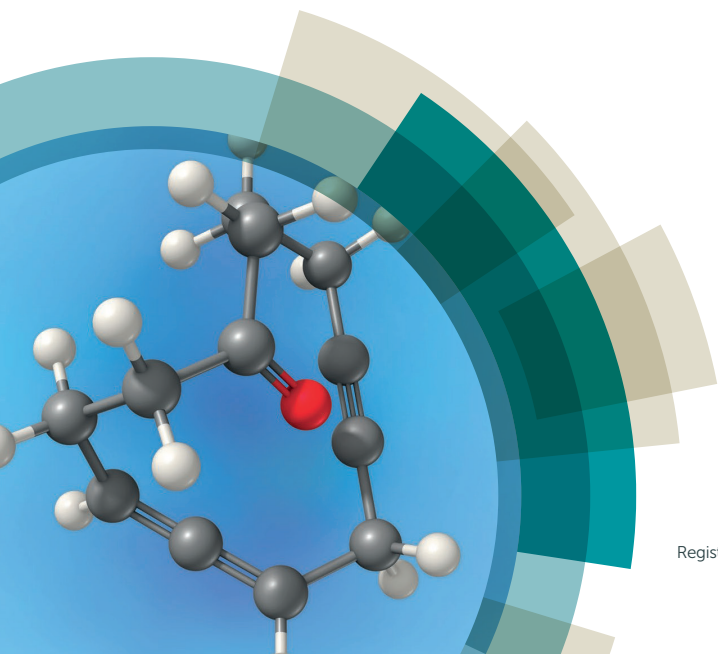
LANZHOU
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23 April 2018, Lanzhou, China

5th Organic Chemistry Frontiers International Symposium

Run Run Shaw Science Building, Lanzhou University

逸夫科学馆，兰州大学



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The 5th Organic Chemistry Frontiers International Symposium

Lecture hall, Run Run Shaw Science Building, Lanzhou University (Panxuan Road Campus)

逸夫科学馆报告厅, 兰州大学 (盘旋路校区)

23 April 2017

Time	Event	Session Chair
9:00-9:15	Opening Remarks Wei Wang (王为), <i>Lanzhou University</i> Daping Zhang (张大平), <i>Royal Society of Chemistry</i>	
9:15-9:45	Aerobic Oxidation, EATA, and Synthesis of Natural Product Shengming Ma (麻生明), <i>Shanghai Institute of Organic Chemistry, CAS</i>	Meixiang Wang 王梅祥 <i>Tsinghua University</i>
9:45-10:15	Total Synthesis of Some <i>Lycopodium</i> Alkaloids Chun-An Fan (樊春安), <i>Lanzhou University</i>	
10:15-10:30	Coffee & Tea	
10:30-11:00	Small Molecules Targeting the Cellular Redox System Jianguo Fang (房建国), <i>Lanzhou University</i>	Xiangfeng Shao 邵向锋 <i>Lanzhou University</i>
11:00-11:30	Transition Metal-Catalyzed Alkyne Functionalization for Use in Organic Synthesis Chulbom Lee, <i>Seoul National University</i>	
11:30-15:00	Lunch & Break	
15:00-15:30	Chiral Bis(guanidino)iminophosphorane as Organosuperbase Catalyst Masahiro Terada, <i>Tohoku University</i>	Frank Würthner University of Würzburg
15:30-16:00	New Tactic to Slice 4-O-5 Linkage in Lignin Models: Palladium-Catalyzed Formal Cross-Coupling of Diaryl Ethers with Amines Huiying Zeng (曾会应), <i>Lanzhou University</i>	
16:00-16:30	Evolution of Cross Coupling Zhangjie Shi (施章杰), <i>Fudan University</i>	
16:30-16:45	Coffee & Tea	
16:45-17:15	Trichalcogenasumanene: Synthesis and Regioselective Transformations Toward Various Non-Planar π-Conjugated Polycycles Xiangfeng Shao (邵向锋), <i>Lanzhou University</i>	Chun-An Fan 樊春安 <i>Lanzhou University</i>
17:15-17:45	Living Supramolecular Polymerization of Organogelators Frank Würthner, <i>University of Würzburg</i>	
17:45-18:15	High Valent Organocopper Chemistry Probed with Synthetic Macrocycles Meixiang Wang (王梅祥), <i>Tsinghua University</i>	
18:15-18:30	Closing Remarks Shengming Ma (麻生明), <i>Shanghai Institute of Organic Chemistry, CAS</i>	



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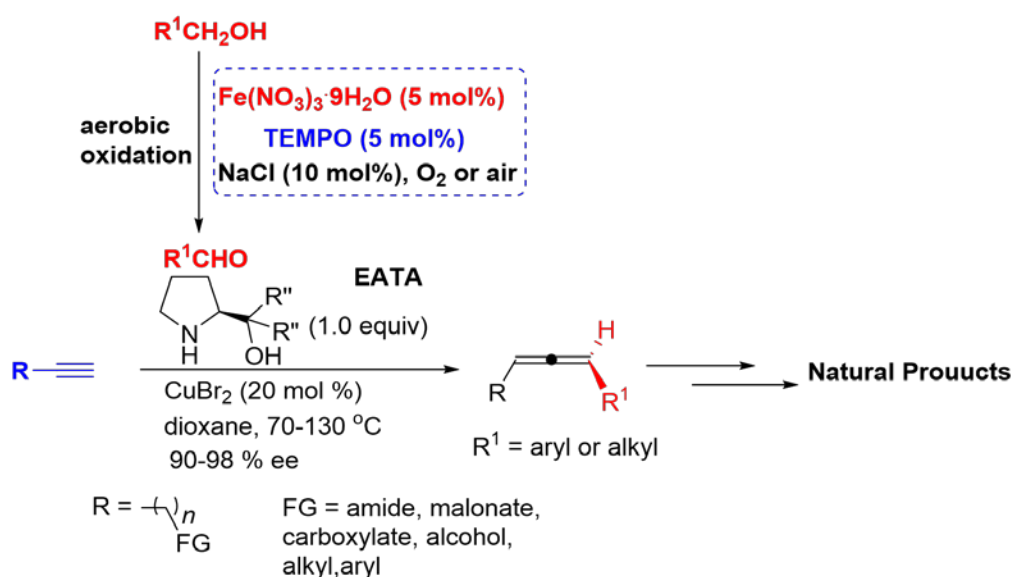
Shengming Ma was born in 1965 in Zhejiang, China. He received his PhD from Shanghai Institute of Organic Chemistry (SIOC) and became an Assistant Professor there in 1991. After postdoctoral research at the ETH with Professor Venanzi and Purdue University with Professor Negishi, he returned to SIOC in 1997. From February 2003 to September 2007, he was jointly appointed by SIOC and Zhejiang University (ZJU). In October 2007, he moved to East China Normal University to help build the research program in organic chemistry. Currently he works as a research professor at SIOC and Qiu Shi Adjunct Professor at ZJU. He received the Mr & Mrs Sun Chan Memorial Award in Organic Chemistry (2004), OMCOS Springer Award (2005), National Award for Research in Natural Science in China (Second-Class, 2006), and Natural Science Awards of Shanghai (First-Class, 2010). He is a member of Chinese Academy of Sciences and TWAS.

Aerobic Oxidation, EATA, and Synthesis of Natural Product

Shengming Ma

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In this lecture, the highly selective aerobic oxidation of primary and secondary alcohols to aldehydes (carboxylic acids) or ketones, enantioselective allenylation of terminal alkynes with aldehydes, and their application to the efficient synthesis of natural products will be presented.



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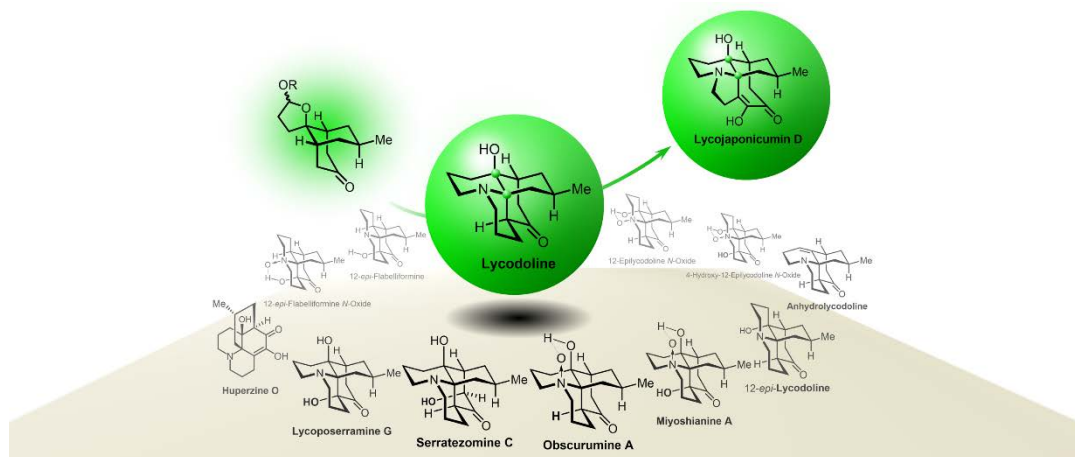
Chun-An Fan, was born in Jiangsu, China. He studied chemistry at Lanzhou University, China, where he received his B.S. in 1999 and completed his Ph.D. with Professor Yong-Qiang Tu in 2004. He then spent one year as a CNRS Postdoctoral Fellow in the laboratory of Professor Henri B. Kagan at Université de Paris-Sud (XI), France. In November of 2005, he joined the group of Prof. Andreas Gansäuer as an Alexander von Humboldt Research Fellow at Universität Bonn, Germany. In November of 2007, he obtained a full professorship position at Lanzhou University, and his current research interests center on the synthetic methodology, asymmetric catalysis, and synthesis of structurally interesting and biologically active molecules.

Total Synthesis of Some *Lycopodium* Alkaloids

Xian-He Zhao, Qing Zhang and Chun-An Fan*

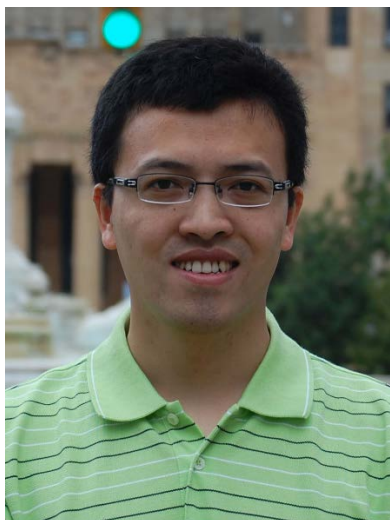
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Natural product synthesis has played a prominent role in the development of the field of organic chemistry by providing a challenging platform for the discovery and invention of new synthetic strategies and methods, which is one of the central issues in modern organic synthesis. With our interest in the synthesis of structurally interesting and biologically active natural products, we recently selected some *Lycopodium* alkaloids¹ as the targets for our synthesis design. Driven by the expeditious construction of the core polycyclic architecture, the design of strategies and methodologies has been explored. Herein we would like to report our efforts to divergent total synthesis of such alkaloids (see below).²



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Prof. Fang received his BS degree in 1998 from the Department of Chemistry, Lanzhou University. He then continued his graduate studies under the supervision of Prof. Zhong-Li Liu, and obtained his PhD degree in 2003. After finishing his postdoctoral training with Prof. Arne Holmgren (Karolinska Institute, Stockholm, Sweden), Prof. Stuart A Lipton (The Burnham Institute for Medical Research, La Jolla, CA) and Prof. Richard B Silverman (Northwestern University, Evanston, IL) from 2003 to 2009, he joined the State Key Laboratory of Applied Organic Chemistry in Lanzhou University as a principal investigator in the March of 2009, and has worked as a full professor since then.

His research interests lie at the interface of chemistry and biology with a particular focus on the biological redox regulation, including development of chemical tools for cellular redox events and target of the cellular redox system for drug discovery.

Small molecules targeting the cellular redox system

Jianguo Fang

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Cellular reduction/oxidation (redox) status controls various aspects of cellular function, and is maintained predominantly by the two intracellular redox-regulating systems, *i. e.*, the thioredoxin system and the glutathione system.¹⁻² Disturbance of the redox homeostasis is associated with an array of pathological conditions and disease states, such as cancer and neurodegeneration.²⁻³ Thus, targeting regulation of the cellular redox status is a promising therapeutic approach for such diseases. We are interested in the discovery of small molecules targeting the cellular redox system, especially the thioredoxin system, as chemical probes or potential drugs.^{2, 4-7} The recent progress in our group will be presented in the symposium.

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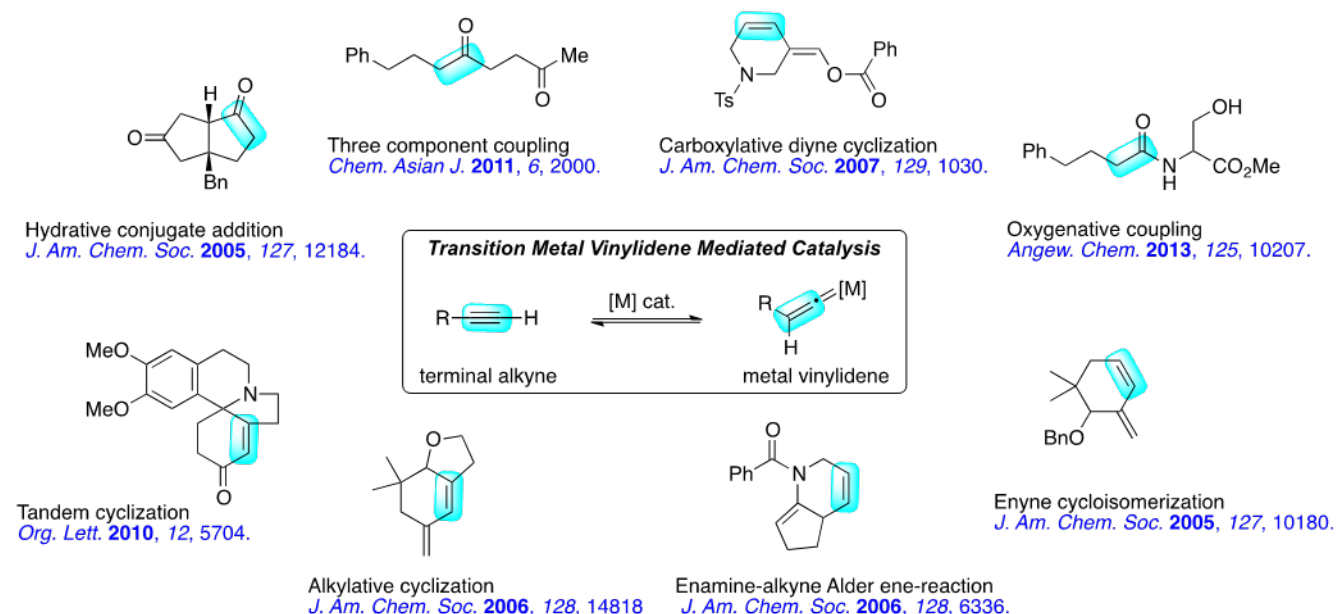
Chulbom Lee obtained his BS & MS degrees from Seoul National University (1988 and 1990), where his advisor was Professor Eun Lee. After military service, he came back to SNU as a Research Associate at the Institute of Basic Sciences. In 1992, he was selected as a National Merit Scholar in Chemistry by the Korean Ministry of Education and went to Stanford University for his PhD studies under the guidance of Professor Barry Trost. In 1998, he moved to Memorial Sloan-Kettering Cancer Center to work with Professor Samuel Danishefsky as a US Army Breast Cancer Research Fellow. In 2001, he joined the faculty of the Chemistry Department of Princeton University as Assistant Professor and in 2008, he moved back to his alma mater, SNU. He is currently Associate Chair of the Department while serving as Vice President of the Korean Chemical Society and the Korean Society of Organic Synthesis. He was the recipient of the Roche Award in Organic Chemistry (1998), the U.S. Army Breast Cancer Research Fellowship (1999-2001), the Thieme Journal Award (2001), the Amgen Young Investigator Award (2006), and the SNU Chemistry Teaching Award (2011). His research is focused on the development of novel reactions and strategies for chemical synthesis.

Transition Metal-Catalyzed Alkyne Functionalization for Use in Organic Synthesis

Chulbom Lee

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Transition metal vinylidene complexes are organometallic species derived from alkynes that are isomeric to σ - and π -alkyne complexes. Our laboratory has been engaged in the development of C–C bond-forming methods that make use of alkynes *via* mechanisms involving a transition metal vinylidene as a catalytic intermediate. A wide range of new reactions has been developed, including enyne cycloisomerizations, and various tandem processes effecting hydrative, alkylative, and carboxylative cyclizations. Recently, in a departure from these C–C bond-forming cyclization processes, our explorations have been focused on the oxygen-transfer to the metal-bound carbene ligand. This approach has led to discovery of the alkyne oxygenation that occur through the intermediacy of a metalloketene species arising from oxidation of the metal vinylidene. Discussed in this talk will be the design, implementation and mechanistic studies of the oxygenative metal vinylidene-mediated catalytic reactions. Also presented will be a novel tandem addition–cyclization–rearrangement process, in which alkyne-tethered hydrazones react with organoboronic acids to give cycloalkane products.¹



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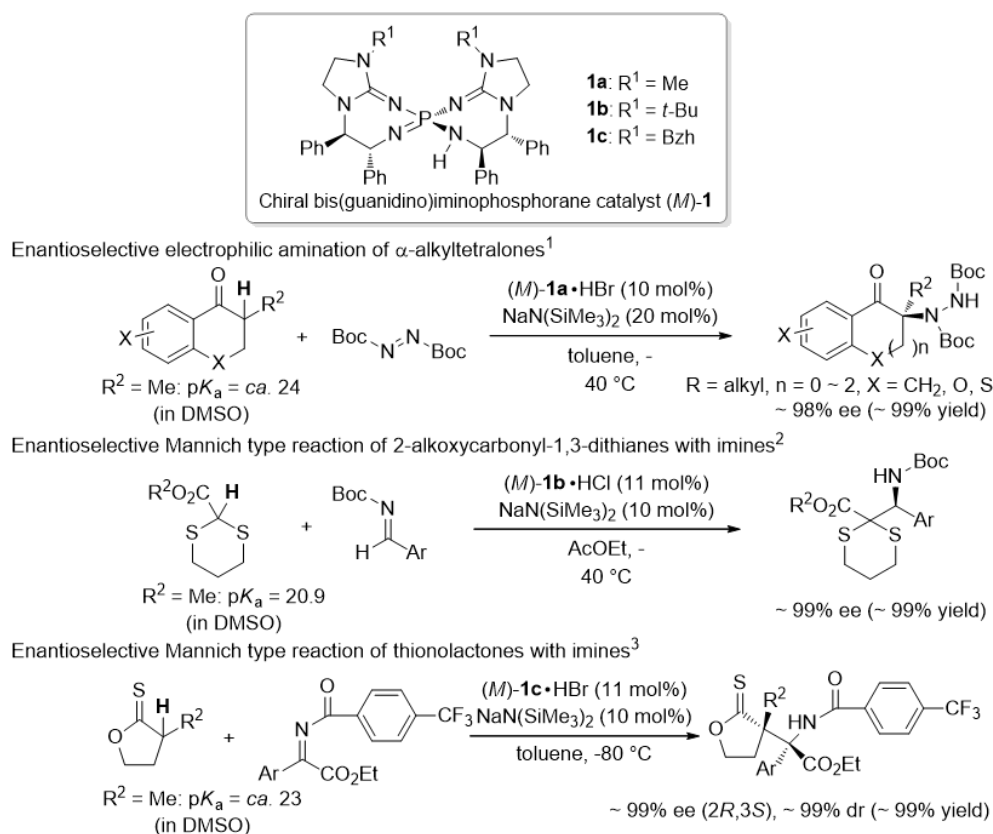
Professor Masahiro Terada was born in Tokyo in 1964. He was graduated from Department of Applied Chemistry, Tokyo Institute of Technology in 1986 and completed his PhD degree in 1993 from Tokyo Institute of Technology under the direction of Professor Koichi Mikami. During his PhD studies, he was appointed as an Assistant Professor in Professor Mikami's Laboratory at Tokyo Institute of Technology (1989-2001). He worked as a postdoctoral fellow with Professor M D Shair at Harvard University in 1999-2000 and moved to Tohoku University as an Associate Professor in 2001. He has been a Professor of Chemistry at the Graduate School of Science, Tohoku University (Japan) since 2006. He is the recipient of the Incentive Award in Synthetic Organic Chemistry, Japan (2003), The Chemical Society of Japan Award for Creative Work (2008), Mukaiyama Award (2010), Daiichi-Sankyo Award for Medicinal Organic Chemistry (2011), and The Nagoya Silver Medal (2012). His current research interests are focused on the development of new and useful synthetic methodologies based on the design of novel chiral Brønsted acid and base catalysts as well as the utilization of transition metal catalysts.

Chiral Bis(guanidino)iminophosphorane as Organosuperbase Catalyst

Masahiro Terada

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Recently, intensive interest has been devoted to the development of chiral uncharged strong organobase catalysts, such as chiral guanidine and P1-phosphazene bases, and these catalysts have been applied to a variety of enantioselective reactions. However, the applications of these catalysts are limited to pro-nucleophiles having a fairly acidic proton, such as 1,3-dicarbonyl compounds and nitroalkanes. In order to overcome these intrinsic limitations, we recently developed a novel chiral bis(guanidino)iminophosphorane **1** as a superb class of uncharged chiral organo-superbase catalysts.¹ In our continuous studies toward expansion of the scope of pro-nucleophiles in organocatalytic reactions, catalytic efficiency of chiral bis(guanidino)-iminophosphorane **1** was demonstrated in several enantioselective reactions of less-acidic pronucleophiles.¹⁻³



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Dr. Huiying Zeng received Ph.D. degree in the State Key Laboratory Elemento-organic Chemistry, Nankai University in 2013, where he studied total synthesis of nature products. He did postdoctoral research in Green Chemistry at McGill University (Canada) in the group of Prof. Chao-Jun Li from 2013 to 2015. He won the Merit Postdoctoral Fellowship (Canada) in 2013-2014. He has been an associate professor at the State Key Laboratory Applied Chemistry, Lanzhou University since 2016. His research interests are mainly focused on catalytic conversion of lignin and related model compounds into aromatic compounds, exploring photo-induced transition metal and photosensitizer free new chemical reaction.

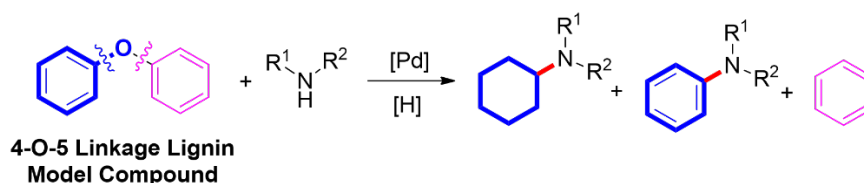
New Tactic to Slice 4-O-5 Linkage in Lignin Models: Palladium-Catalyzed Formal Cross-Coupling of Diaryl Ethers with Amines

Huiying Zeng*, Dawei Cao and Chao-Jun Li

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Conversion of renewable resources into higher value-added organic chemicals is becoming more and more important for our society's future sustainable development. Lignins, being the second abundant organic carbon renewable resources on Earth, have been treated as waste in the pulp and paper industry. The 4-O-5 linkage diaryl ether bond, is the strongest linkage among three types of ether linkages in lignins. Selective cleavage of this linkage can potentially generate smaller processible bio-based aromatic polymeric materials and compounds.¹ Furthermore, there has been a long synthetic interest in coupling reactions with aryl ethers *via* C(Ar)-O bond cleavage, for example for polyphenylene oxide (PPO) waste recycling. Up to date, the 4-O-5 ether linkage model compounds have been cleaved to obtain phenol, cyclohexane, cyclohexanone, and cyclohexanol.²

In this talk, the first example of direct formal cross-coupling of the 4-O-5 linkage model compounds, diaryl ethers, with amines *via* dual C(Ar)-O bond cleavages to generate valuable nitrogen-containing derivatives will be introduced.³ Both symmetrical and unsymmetrical diaryl ethers were successfully cross-coupled with amines *via* a dual C(Ar)-O bond cleavage, providing a model for selective lignin 4-O-5 linkage modification.



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Professor Shi received a BS degree in 1996 from the Department of Chemistry, East China Normal University. He joined Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences (SIOC, CAS) and obtained his PhD degree (2001) under the supervision of Professor Shengming Ma. He then moved to Harvard University as a Postdoctoral Researcher with Professor Gregory Verdine and later became a Research Associate with Professor Chuan He at the University of Chicago. He joined the faculty of College of Chemistry and Chemical Engineering, Peking University at the end of 2004 and was promoted to Full Professor in 2008. In 2017, he moved to Fudan University and continue his research career there. Owing to his contributions in this field, Dr Shi is a recipient of OMCOS Award at 2013 and Tetrahedron Young Investigator Award at 2011.

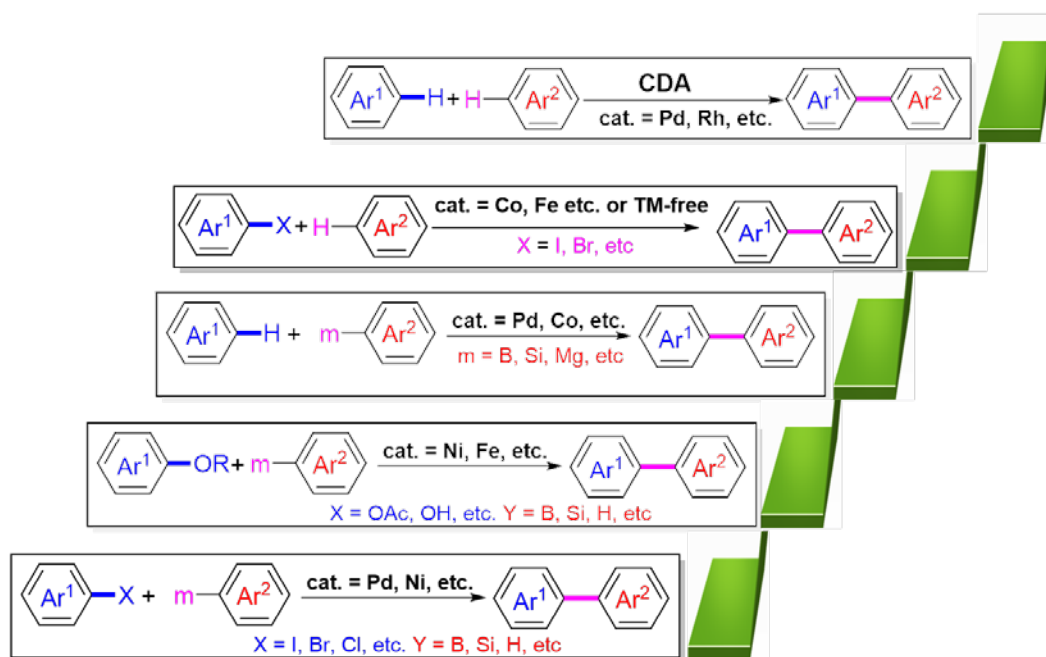
His research interests were focused on organometallic chemistry and catalysis, especially in the field of the activation of "inert" bonds and small molecules.

Evolution of Cross Coupling

Zhang-Jie Shi

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Conventional cross coupling is one of the most powerful methods to construct carbon-carbon bonds starting from organohalides and organometallic reagents, catalyzed by late transition-metal catalysts in general.¹ With our and others' efforts, the electrophilic partner can be taken place of by O-based electrophiles.² C-H bonds could also applied as coupling partners, coupled with various organometallic reagents, as well as another molecule of C-H bonds.³ To avoid the utilization of late and heavy transition-metal catalysts, the earth-abundant transition-metal and even metal free catalytic systems were built up to proceed the cross coupling between organohalides and arenes.⁴ These studies may lead the evolution of cross coupling in an environmentally benign manner.



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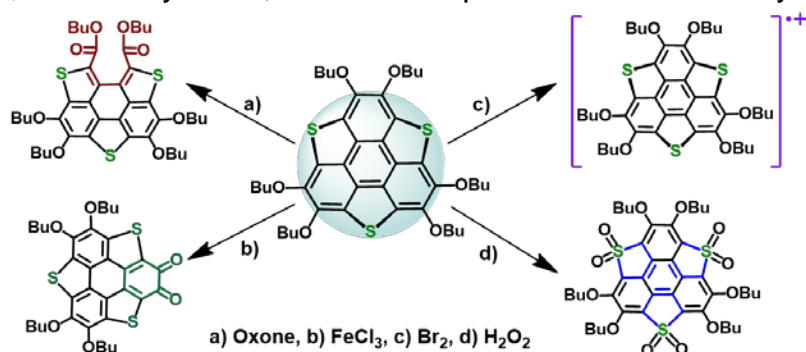
Xiangfeng SHAO was born in Gansu Province of China in 1977. He received the B.S. (1998) and M.S. (2001) degrees in chemistry from Lanzhou University (LZU), where his advisor was Professor Zhongli Liu. He further joined Institute of Chemistry, Chinese Academy of Sciences (ICCAS) and obtained his PhD degree (2004) under the supervision of Professor Daoben Zhu. He then moved to Japan to carry out the postdoctoral research in Japan Science and Technology Agency (JST), Kyoto University, and Osaka Prefecture University. During that period, he mainly focused on the innovation of multifunctional organic conductors based on charge-transfer complexes. In 2009, he returned to his alma mater, LZU, to take a position at the State Key Laboratory of Applied Organic Chemistry (SKLAOC). In 2015, he received the “Excellent Young Scientists Fund” from National Natural Science Foundation of China (NSFC). His research interests include the physical organic chemistry, synthesis of curved pi-systems, supramolecular architecture, and optoelectronic properties of organic materials.

Trichalcogenasumanene: synthesis and regioselective transformations toward various non-planar π -conjugated polycycles

Yantao Sun, Xueqing Hou, Shitao Wang, Ruili Geng and Xiangfeng Shao*

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Sumanene is a C_{3v} -symmetric buckybowl showing interest in chemistry and material science. By introducing hetero atoms into conjugated core of sumanene, one may finely tune the electronic and assembling features of the resulting heterasumanenes.¹ Herein, we report our recent progress on trichalcogenasumanenes (**TCSs**) which are generated by replacing benzyl carbons on sumanene with chalcogen atoms (S, Se, and Te). These **TCSs** were synthesized from hexabutoxytriphenylene through non-pyrolytic approach.² The **TCSs** are electron-rich and have three active sites, the outer C=C bond, chalcogen atoms, and the butoxy groups. By screening reagents, we successfully carried out the regioselective transformation on **TCSs** (**Scheme 1**), and the successive functionalization toward molecular spoons, chiral π -systems, and chiral supramolecular assembly.³



Scheme 1. Regioselective transformation of trithiasumanene

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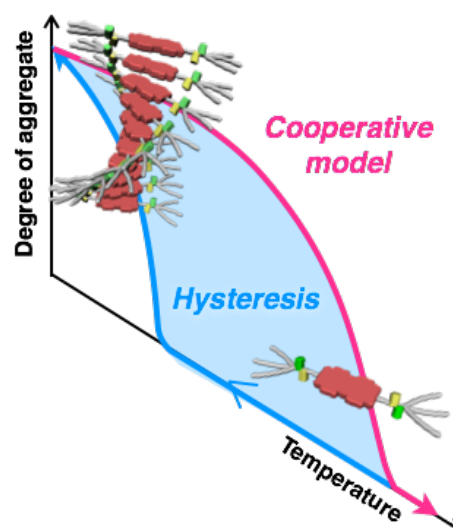
Frank Würthner received his education and PhD degree (1993) at the University of Stuttgart (Germany). He was a Lynen Fellow of the Alexander von Humboldt foundation and carried out postdoctoral research at MIT in Cambridge/MA (USA). After two years in the BASF central research laboratories in Ludwigshafen (Germany) he moved to the University of Ulm where he received the Habilitation in 2001. Since 2002, he is Chair Professor at the University of Würzburg, where he has served as Head of the Institute of Organic Chemistry, Dean of the Chemistry and Pharmacy Department and Founding Director of the Center for Nanosystems Chemistry. His main research interests include the synthesis of pi-conjugated molecules and functional dyes, their application in organic electronics, photonics and photovoltaics, the construction of complex supramolecular architectures composed of pi-scaffolds, and the investigation of light-induced processes in dye-based nanosystems. He has published more than 300 papers and is among the most highly cited chemists of the last decade.

Living Supramolecular Polymerization of Organogelators

Frank Würthner

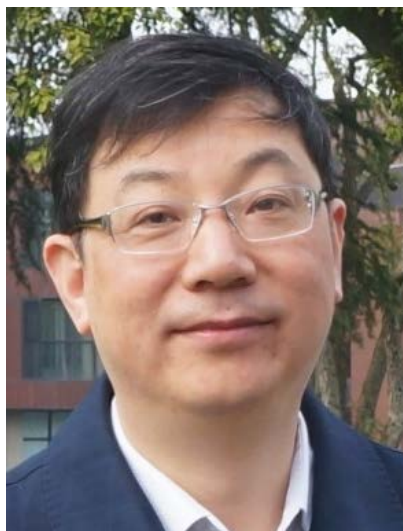
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During the last decade a multitude of organogelator molecules have been reported. In general the gelation process is described as a supramolecular polymerization directed by intermolecular forces among which hydrogen bonding and π - π -stacking are the most prominent ones. Mechanistic insights into the fiber growth and subsequent gelation process remained, however, scarce. In our recent studies we were able to clarify the mechanism of supramolecular polymerization for archetype organogelator molecules composed of perylene bisimide aromatic scaffolds and two amide substituents.^{1,2} These molecule self-assembles into elongated one-dimensional nanofibers through a cooperative nucleation-growth process. Thermodynamic and kinetic analyses revealed conditions (temperature, solvent, concentration) where the spontaneous nucleation is retarded by trapping of the monomers in an inactive hydrogen-bonded conformation, leading to lag times up to more than one hour. The unique kinetics in the nucleation process was confirmed as a thermal hysteresis in a cycle of assembly and disassembly processes. Under appropriate conditions within the hysteresis loop, addition of pre-assembled nanofiber seeds leads to seeded polymerization from the termini of the seeds in a “living” supramolecular polymerization process.³ In our most recent work these seeds could be utilized to prepare block co-polymers composed of H- and J-aggregated perylene bisimide domains.



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Professor Meixiang Wang received a BS degree in 1983 from the Department of Chemistry, Fudan University. After spending 3 years in General Research Institute of Non-ferrous Metals as a research associate, he joined Institute of Chemistry, Chinese Academy of Sciences (ICCAS) at Beijing as a research student. He obtained his master degree (1989) and PhD (1992) under the supervision of Professor Zhi-Tang Huang. He then worked at ICCAS for the next 17 years, ranking from Assistant Professor, Associate Professor and Professor. During 2000 to 2004, he served as the Director of ICCAS and the Director of CAS Center for Molecular Sciences. From the May of 2009, he has been Professor of Organic Chemistry at Tsinghua University.

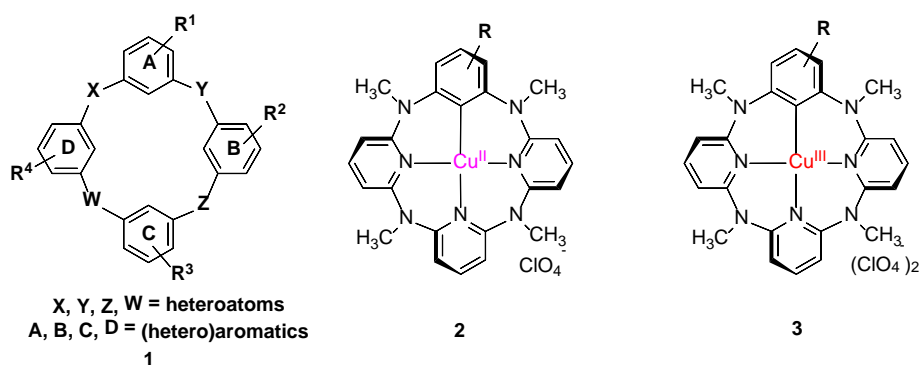
His research interests include supramolecular chemistry of novel heteroatom-bridged calixaromatics, enantioselective biotransformations using whole cell catalysts, and selective organic reactions for the synthesis of bioactive compounds.

High Valent Organocopper Chemistry Probed with Synthetic Macrocycles

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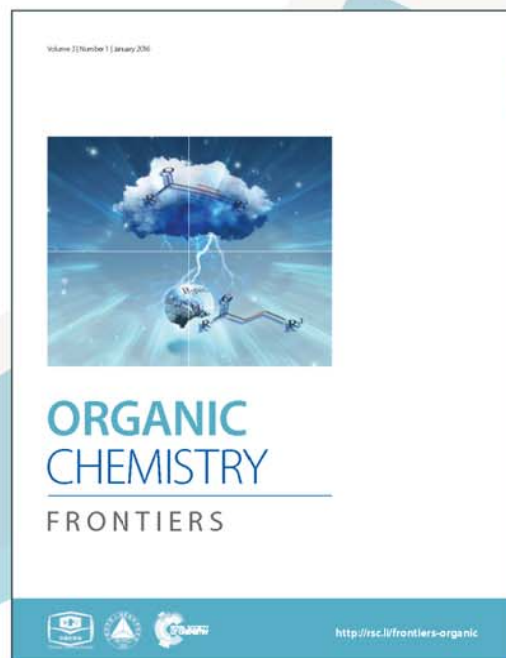
Copper-catalyzed and mediated cross coupling reactions are one of the most frequently used methods in the synthesis of carbon-carbon and carbon-heteroatom bonds. Recently, copper catalysis has also been shown to be a promising strategy in C-H bond activation and functionalization. Despite the wide applications of copper salts in catalysis, reaction mechanisms have remained elusive owing to the difficulty in identifying the structure and reactivity of organocopper species involved in organometallic reactions. Using heteracalixaromatics (**1**), a type of synthetic macrocycles in which the multiple and convergent coordination sites are readily designed, we were able to selectively synthesize an array of structurally well-defined high valent arylcopper(II) (**2**) and arylcopper(III) compounds (**3**). Synthetic macrocycles and their organocopper complexes of different oxidation states provide us with unique and powerful molecular tools to probe the details of copper-catalyzed or promoted direct arene C-H bond transformations. In this talk I will summarize the recent advance of our study on high valent organocopper chemistry with emphasis on the mechanism of cross-coupling reaction of arene C-H bond with anionic carbon and heteroatom nucleophiles and with boronic acids.



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