Publication Date (Web): March 10, 2014 | doi: 10.1021/bk-2014-1157.ch012

Chapter 12

Chemical Sciences: Contributions to Building a Sustainable Society and Sharing of International Responsibilities

Zhigang Shuai,*,[1] Xi Zhang,[1] and Jiushu Shao[2]

[1]The Chinese Chemical Society and Department of Chemistry, Tsinghua University, 100084 Beijing, China
[2]School of Chemistry, Beijing Normal University, 100875 Beijing, China
***E-mail: zgshuai@tsinghua.edu.cn**

In this report, we first demonstrate that chemistry is the central science from the science of matter to the science of life; i.e., chemistry is essential for food supply and resources, for understanding life processes, for providing clean and renewable energy, for material science, for information technology, and for environmental sciences. Then, we summarize the recent advances in chemical sciences in China, in nano science and technology, material chemistry, supramolecular self-assembly, organic synthesis, and more fundamentally physical and theoretical chemistry. Chinese chemists have not only made significant progress in chemical research but also assumed international responsibility in tackling globally challenging problems by collaborating with international chemists and providing chemical solutions to energy, environment, health, and resources problems. Lastly, we present some remaining challenges in chemical sciences and our perspectives on the contributions that chemistry can make towards a sustainable and harmonious society.

Cheng et al.; Vision 2025: How To Succeed in the Global Chemistry Enterprise
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

Introduction

Chemistry is a science that studies all types of substances, including atoms, molecules, supramolecules, and other large molecular and solid systems. The focus in the field tends to be on syntheses, transformations, isolation, analyses, structural and conformational determinations, and physical and chemical properties of substances. As the most important field that can create new substances, chemistry not only is a central part of fundamental sciences, but also has a broad spectrum of applications. On one hand, chemistry helps us understand why molecules in nature are what they are and tells us how to construct novel substances unavailable in nature. On the other hand, chemistry is essential to material civilization and dramatically improves the quality of life for human beings by providing new materials for numerous applications. Because chemistry is at the center of natural sciences, its advances directly influence biology, medicine, agriculture, materials, and other related areas. There is no doubt that chemistry will continue to play a unique role in advancing developing countries and in building a sustainable and harmonious world.

The development of chemical sciences in all their facets is astonishing. Tens of millions of molecules and compounds have been synthesized and their structures at atomic scale have been elucidated. Novel techniques and synthetic methodologies have been developed, which pave the way to the manufacturing of new materials with targeted properties. In addition to offering methods for the creation of new substances, chemistry also reveals how and why transformations of matter or chemical reactions take place. In fact, the structures and dynamics of chemical systems are favorite research topics in modern chemistry. In view of the principle that structures determine properties, chemical knowledge helps establish structure-property relationships of substances at the molecular, supramolecular, aggregate levels, and beyond, thus achieving the ultimate goal of rational design of new molecules, new drugs and other new substances.

Chemistry has changed the world and benefitted human beings in many ways. A good example is the high-pressure catalyzed process for ammonia synthesis, which allowed large-scale man-made fertilizers to be made. It was one of the most important inventions in the twentieth century, and has revolutionized agricultural production. Another example is oil refinery. The application of highly efficient platinum catalysis has produced vast amounts of high-quality gasoline and aromatic hydrocarbons that are needed by industry. Thanks to chemists' efforts, various analytical instruments are available and are widely used to monitor the environment, and pollution can be effectively traced and controlled accordingly.

The origin of life is one of the most challenging problems in science. Biological processes are complicated due to highly ordered combinations of chemical reactions. The clues to to this complex problem can only be found by studying the chemistry of living things.

Indeed, chemists are getting more and more interested in complex systems at multiple scales. They establish state-of-the-art experimental and theoretical methodologies to explore the structures, dynamics, and functions of the systems. In addition, computers have been extensively employed in modern chemistry, for information storage and analysis, data mining, and theoretical modeling of chemical phenomena. A successful example is the computer-assisted drug design, which tremendously saves money and time when compared with the traditional trial-and-error approach.

Modern chemical sciences have advanced to an unprecedented level, and many tools and methodologies are now available. Certainly chemistry can be used to create new substances to meet the changing needs of human beings. Moreover, the development of new chemical ideas and methods has helped life sciences, material science, and even information technology. Today we are facing global challenges in exploring energy and other resources, in protecting environment, in coping with global warming, in addressing health and medical issues, in maintaining a sustainable world, and many others. The following pages outline the different roles that chemistry can play in addressing these global challenges.

Publication Date (Web): March 10, 2014 | doi: 10.1021/bk-2014-1157.ch012

1. Chemistry is one of the key sciences for solving the world's food supply and resources problem.

China is an agriculture-intensive country. A strong agriculture is necessary for a healthy national economy and a guarantee of a stable government. The total population in China will reach 1.6 billion by the middle of this century. It is a formidable task to provide sufficient food supply for this large population and at the same time to protect the agro-ecological environments. Chemistry contributes to the manufacturing of highly efficient and yet environmental friendly fertilizers, pesticides, and plastic membranes for agricultural production. In particular, chemistry is used to design and produce green bio-fertilizers, bio-pesticides, and biodegradable materials. Chinese chemists have made enormous efforts in maintaining and treating soil pollution, desertification, drought, as well as salinization and other cultivation and ecological problems. Both Chinese chemist and scientist from other disciplines will explore the mechanism of the photosynthetic reactions of plants, which will be invaluable as we try to increase the agricultural production via genetic and genomic engineering.

2. Chemical process is fundamental for understanding life so that chemistry can ensure the living standard and health of humankind.

Chemists and the chemical sciences have been integral to the development of modern medicine, from drug compounds to drug delivery systems to diagnostic technologies. The result has been a steady improvement in our health and life expectancy over the past 100 years. Complex chemical processes are involved in the life processes including growth, reproduction, aging, disease, death and so on. The research activities therein are dependent on chemical theory, techniques and methodologies at the molecular level. Chemistry of life, including chemistry of brain and memory is a big challenge and of utmost importance. One can never overestimate the importance of chemistry in medicine. Chemists invent new medicines such as antiviral and antibiotics to relieve pain caused by sickness and to cure diseases. They improve new diagnostic methods so that diseases can be detected, identified, and treated at an early stage. They are also developing biocompatible materials for organ transplant.

3. Chemistry is essential for providing clean and renewable energy for the future.

Energy is essential to us. We need energy for manufacturing, transportation, heating, lighting, and daily life. In China, more than 90% of energy utilization rely on chemical processes. It is a great challenge for chemists to design effective chemical processes to transform the low-quality fuels to energy at low costs and reduced pollution. Fossil fuels, including coal, petroleum, and natural gas, are limited in resource and cannot be regenerated. With current technology, the burning of fossil fuel produces a large amount of oxides of sulphur and nitrogen, and other pollutants. Therefore, while efforts in more efficient and cleaner conversion of fossil fuels should be sought, new energy sources should be researched. Chemists need to develop new tools, concepts, and technologies to explore solar energy, nuclear energy, hydrogen and fuel cells, and others.

4. Chemistry consists of the source of materials sciences.

Materials are needed for a wide variety of applications. The national economy, industrial modernization, and national defense all benefit from the developments of new or improved materials. Chemists make new materials by synthesizing new compounds and characterizing their structures and properties. At the atomic, molecular, and supramolecular levels, chemical sciences help to design materials with required optical, electrical, magnetic, and mechanical properties. By virtue of the structure-property relationships, molecular scientists can apply the rational design strategy to develop new generations of semiconductors, optical materials, magnetic materials, superconductors, high temperature heat resistant matters, super-hard materials, and other advanced materials. From synthesis to processing to commodity manufacturing of materials, the tools of chemical science and engineering will be essential. New materials with predictable properties will provide formidable targets for design and synthesis, while processing and manufacturing of these new materials will present new challenges and opportunities for chemical engineering.

5. Chemistry in Information Technology

Information technology is a strong pillar for the 21st century industry. The fast growth and widespread application of internet communication technology has a tremendous impact on human life. Chemistry not only provides basic substances for information generation, transmission, storage, and display, but also provides new materials and manufacturing processes for ultra-large scale integration circuits. Miniaturization of device will ultimately reach molecular size. Electronic devices at molecular level and biochips are among the most rapidly growing areas with an intense focus in chemistry. Among them, molecular wires, molecular switches, molecular motors, and molecular rectifiers have achieved great success recently. The development of scanning probe microscopy (SPM) allows chemists to study single atom, single molecular behavior, as well as electronic device performance at molecular scale.

6. Chemistry can provide tools and methods to address environmental problems.

As the population increases, urbanization spreads extensively, energy consumption soars, and pollution in water, atmosphere, and soil becomes very serious. Chemists need to find economically viable reactions and design environmentally benign reaction processes that can be scaled up from laboratory to industry. Green chemistry is the ultimate solution. In addition, chemists need to understand the chemical compositions and physical phenomena of the earth. They need to understaned the chemistry that occurs in rivers, lakes, oceans, and atmosphere as well. With improved knowledge, chemists can tackle environmental problems. For instance, they can 1) establish highly sensitive detection methods to monitor the migration and transformation of pollutants. 2) Develop efficient and clean approaches for fuel burning. 3) Design suitable processes to remedy polluted water and soil. Of course, chemists should be responsible for instituting and revising the standards for environment protection management.

In summary, chemical sciences not only made great contributions in the past, but also await a more exciting future. As chemists, we should be ready to meet the ever-increasing challenges in managing the world's resources, energy, water, climate, and environment.

Recent Advances in Chemical Research in China

The year 1978 was called "Springtime for Science in China" and a very special year in the scientific history of China: The authorities of the Central Government started to recognize that science and technology are the main driving forces for China's modernization and inaugurated an unprecedented National Science Conference. Since then, the scientific endeavors in China have progressed at a rapid pace. The warmth of the Springtime hopefully will continue to be beneficial to the scientific research and development in China, and at the same time it will bring big rewards. The growth of chemical sciences in China is reflected by the increase in the number of publications. According to the statistics from Chemical Abstract (CAplus), China has always ranked No. 1 in terms of total number of publications in chemistry for the period of 2006-2010 shown in Table 1.

In fact, since 1996 many Chinese scientists have returned home with research experiences, either in Ph.D. programs and/or as postdocs in US, Europe, and Japan. To attract more young and experienced scientists from abroad, the Chinese Academy of Sciences and some elite Chinese universities have launched various "Talent Search Program" since then. The most successful example is the so-called "Hundred Talents Program" supported by the Chinese Academy of Sciences. Since 1995, about 2500 scientists from US, Europe, Japan, and other countries have joined its research institutes and many of them have become leading figures in their fields. Besides, the National Natural Science Foundation of China (NSFC), the most important funding agency for basic science in China, started the "Outstanding Young Scientist Award" (OYSA) program in 1994, aiming at

Cheng et al.; Vision 2025: How To Succeed in the Global Chemistry Enterprise
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

supporting potential Chinese scientists under age 45 to start up their ambitious research groups. The OYSA program has been extremely successful and has been considered as a great honor for all young Chinese scientists. In particular, each awardee receives a considerable amount of funding for a period of 4 years. About 500 young chemists have won OYSA awards until now and they have become the research leaders responsible for developing chemical sciences in China.

Table 1. Top 10 countries in terms of total publications in Chemistry for 2006-2010[1]

Country	*2006-2010*	*Rank*	*Proportion*	*Growth rate*
P. R. China	117420	1	18.59%	14.35%
USA	114514	2	18.13%	2.13%
Japan	52978	3	8.39%	-1.19%
Germany	48265	4	7.64%	1.56%
India	38920	5	6.16%	8.21%
France	33309	6	5.27%	1.26%
England	31126	7	4.93%	0.11%
Russia	28553	8	4.52%	-1.10%
Spain	24983	9	3.96%	3.23%
S. Korea	21933	10	3.47%	7.47%

[1] From CAplus

Undoubtedly, it is the people making all scientific achievements possible. It is also true that the performance and breadth of talented scientists, especially experimentalists, can be greatly enhanced with strong support. The story is the same in China: scientific research and scientists benefit a lot from the booming economy. The funding for basic science has been increased more than 10 folds during the past 15 years. Tremendous improvements have been achieved in terms of laboratory facilities, space and conditions, and the workforce. As noted by Professor Peter Stang of the University of Utah, Editor of the Journal of the American Chemical Society: that "Chinese chemists are already world class in some areas." Indeed, some top-level chemistry research institutions such as the Institute of Chemistry of the Chinese Academy of Sciences and the College of Chemistry and Molecular Engineering of Peking University aim at becoming world first-class research centers for chemical sciences within 10 years. To this end, these two institutions decided to unite their forces to form the Beijing National Laboratory for Molecular Science (BNLMS), which has obtained strong support from the Ministry of Science and Technology of China with an annual budget of about 6 millions USD.

J. Am. Chem. Soc. and Angew. Chem. Int. Ed. are widely regarded as the top chemistry journals. The following charts (Figure 1 and Figure 2) show the impressive increases for the papers in these two journals published by Chinese chemists in the period of 2000 - 2012.

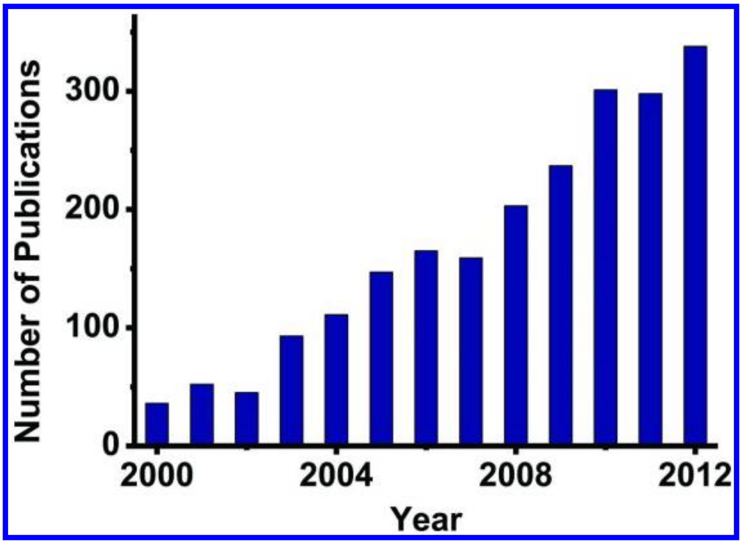


Figure 1. Yearly publications in JACS by Chinese chemists. (from Essential Science Indicators Web of Science.)

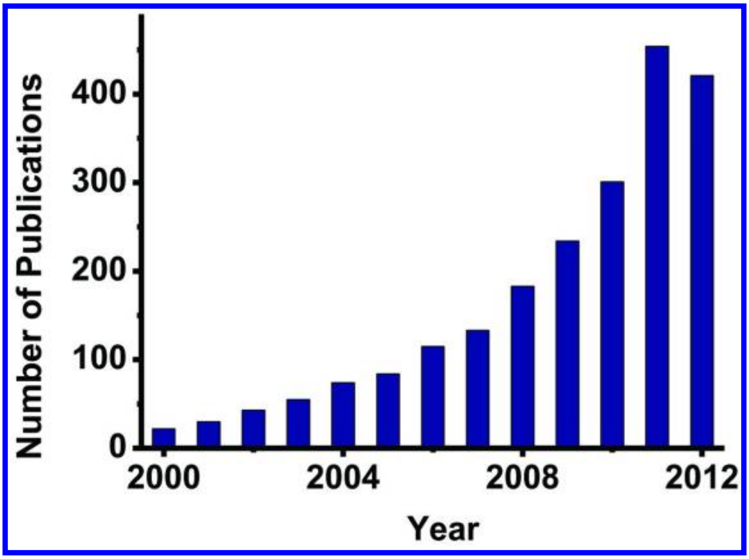


Figure 2. Yearly number of publication in ACIE by Chinese chemists. (from Essential Science Indicators Web of Science.)

It is evident that not only the quantity, but also the quality greatly improved in the past decades. This is also manifested by the total number of citations (see Table 2).

Table 2. Total number of citations for chemistry papers in the period of 2006-2010. (from Esential Science Indicators Web of Science)

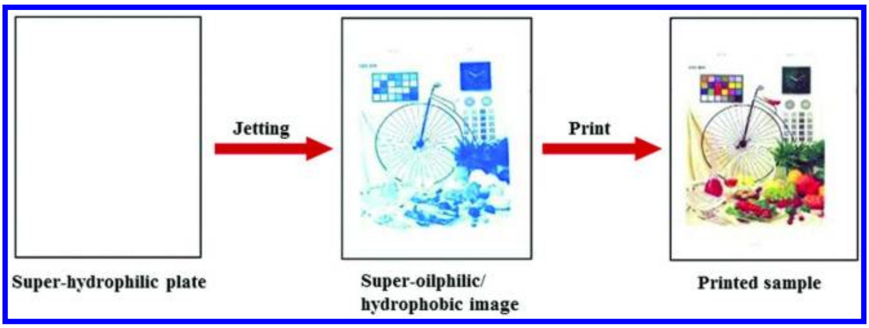
Country	2010	2006-2010	Rank
USA	20872	990901	1
P. R. China	10085	466396	2
Germany	7682	345650	3
Japan	5177	300426	4
England	5372	233100	5
France	4146	212280	6
Spain	3256	166266	7
India	3083	142638	8
Italy	2714	134302	9
Canada	2316	119582	10

It is not the purpose of this report to make an overall assessment on the chemical research progress from China. We intend to present some representative research results in China in nano-science, molecular and supramolecular self-assembly, chemistry of advanced materials, environmental chemistry, organic synthesis, and fundamental physical and theoretical chemistry.

1. Advances in Nano-Science

An important milestone of nanoscience in China is the development of home-made scanning tunneling microscope (STM) by Prof. Chunli Bai from the Institute of Chemistry of the Chinese Academy of Sciences. In the mid-1980s the STM was not yet commercially available. He successfully designed and developed not only the very first STM, but also the first atomic force microscope (AFM), low-temperature STM, ultra-high vacuum-STM and the ballistic electron emission microscopy (BEEM) in China. Indeed, these were the earliest technological tools in the country for characterizing and manipulating single atoms and molecules as well as surfaces and interfaces in the nano-scale world. These achievements marked the birth of scanning probe microscope (SPM) research and opened the door to nanoscience research in China. Owing to Bai's efforts, nanoscience has been a fast growing field in the last twenty years.

Print industry is one of the backbone industries in China; however, it produces a large amount of solid waste, air emission, and wastewater. In order to avoid the complex multi-step processing of laser typesetting plate-making and serious pollution of traditional printing industry based on photosensitizing process, Prof. Yanlin Song from the Institute of Chemistry of the Chinese Academy of Sciences invented a non-photosensitizing, non-pollution and low-cost green plate-making technology (*1*, *2*). Based on the manufacturing of functional nanomaterials, controllable spreading and transferring of liquid droplets, they fabricated the superoleophilic patterns on the hierarchically structured superhydrophilic plate by ink-jet printing (*3*, *4*). Since, the the photosensitizing process is completely avoided, the new technology simplifies the chemical engineering process, discharges no chemical pollluants, and reduces cost (Scheme 1). In a step forward, they employed such green printing technology to printing electronics based on metal nanoparticle ink, which simplifies the traditional photolithography method, and reduce discharge of chemical pollutant (*5*). The necessary technologies for the green plate-making and printing as-a-whole have been pooled together. Pilot lines have been established, which has an annual production capability of millions of square meters of printing plates and tens of metric tons of nanomaterials.



Scheme 1. Schematic demonstration of the production process, which shows that no photosensitizing process is involved in this new technology and the printing plate is directly obtained by inkjeting functional nanomaterials on the superhydrophilic plate to achieve desired superhydrophobic image area.

The ultimate goal of chemistry is to shape the world at the single molecular level. Among all properties of matters, the magnetism of a single molecule is particularly interesting because of its potential applications in future molecular scale information storage and quantum devices. Profs. Jianguo Hou, Jinlong Yang and coworkers from the University of Science and Technology of China reported the first example of manipulating the magnetism of a single molecule with a scanning tunneling microscope, an extraordinary example of bond-selective chemistry (*6*). It is known that there is an unoccupied spin in a free cobalt phthalocyanine molecule, but the magnetism is completely quenched when the molecule is adsorbed on an Au (111) surface. Cutting away eight hydrogen atoms from the molecule with voltage pulses from a scanning tunneling microscope tip

Cheng et al.; Vision 2025: How To Succeed in the Global Chemistry Enterprise
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

allowed the four lobes of this molecule to chemically bond to the gold substrate, and the localized spin was then recovered in this artificial molecular structure (see Figure 3). This beautiful experiment was highlighted by the Science magazine, which reported "*the result opens the way for fundamental studies of spin behavior in molecules that may influence future molecular device applications*". The work clearly *demonstrates an ability to change the magnetic state of a molecule by directly modifying its structure via single-molecule manipulation*; it *takes such manipulations to a new level*.

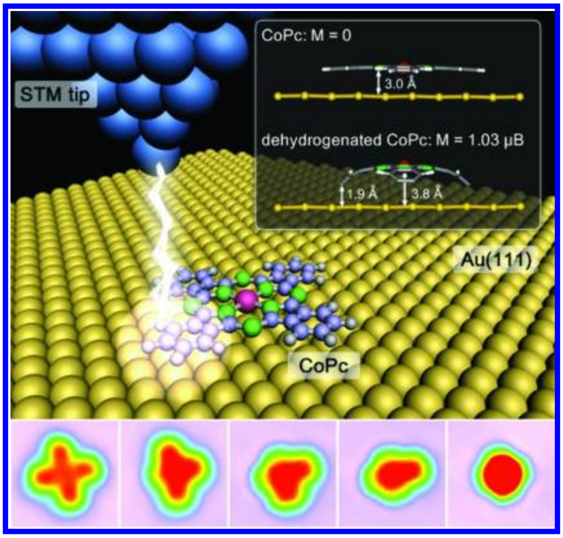


Figure 3. Illustration of manipulating single molecule magnetism. (see color insert)

Because of the complexity of structures and properties of different materials, it is extremely difficult if not impossible to develop a universal methodology for the controlled growth of low-dimensional nanostructures. Prof. Yadong Li of Tsinghua University has invented an all-around method, namely the liquid-solid-solution phase transfer and separation process, for creating nanocrystals (*7*). Their synthetic scheme was based on a general phase transfer and separation mechanism occurring at the interfaces of the liquid, solid and solution phases present during the synthesis (Figure 4). This method can be feasibly used to produce nanocrystals of noble metals, semiconductors and conducting polymers, that is, magnetic, dielectric, fluorescent, optoelectronic or biomedical nanocrystals. This novel synthetic procedure enables much progress in understanding the intrinsic size-dependent properties in different systems of nanocrystal building blocks and drives more unique and exciting applications in the bottom-up nanotechnology.

Prof. Lijun Wan from the Institute of Chemistry of the Chinese Academy of Sciences has made remarkable contributions in controlling the distribution and dispersion of organic/biomolecules on solid surfaces, which is indispensable for nanomaterials and nanotechnology. Using self-assembled technique,

Cheng et al.; Vision 2025: How To Succeed in the Global Chemistry Enterprise
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

he has successfully fabricated a molecular template of end-functionalized oligo(phenylene-ethynylene) (OPE). The structure and molecular arrangements in the template were clearly determined by the electrochemical STM. With the molecular template, organic molecules such as coronene (COR) and biomolecules such as tripeptides are well distributed and are monodispersed on highly oriented pyrolytic graphite (HOPG) surfaces. COR molecules were controllably distributed into the template and self-organized into various arrays by simply adjusting the molecular molar ratio. Recently, they reported the induction of global homochirality in two-dimensional enantiomorphous networks of achiral molecules via co-assembly with chiral co-absorbers. The STM investigations and molecular mechanics simulations demonstrate that the point chirality of the co-absorbers transfers to organizational chirality of the assembly units via enantioselective supramolecular interactions and is then hierarchically amplified to the global homochirality of two-dimensional networks (*8*).

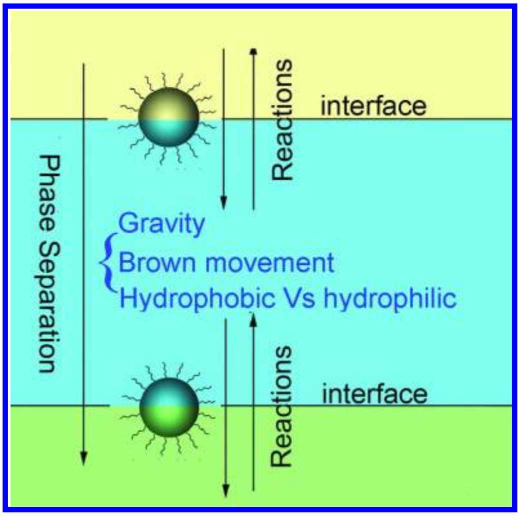


Figure 4. A novel general synthesis method for nanocrystals. (see color insert)

While stable fullerenes, such as C_{60} and its larger homologs, have been macroscopically synthesized since 1990, the fullerenes smaller than C_{60} are highly reactive and have eluded us for twenty years. As an important achievement in the smaller fullerene synthesis, a group of researchers led by Lan-Sun Zheng at Xiamen University in China stabilized an elusive C_{50} cage in milligram amounts by chlorination (*9*). The structure of $C_{50}Cl_{10}$ was characterized by mass spectrometry and nuclear magnetic resonance (NMR), and confirmed by X-ray crystallography recently (Figure 5). This research group initiated their studies on carbon clusters in gas phase since 1980s, and entered the scientific field of macroscopic synthesis of fullerene-related compounds in 1990s. Utilizing various plasma-generating technologies combined with chlorination reactions, they have now been able to synthesize a series of chlorinated derivatives of other labile fullerenes, e.g., C_{54}, C_{56}, C_{58} and isomeric C_{60}'s. These works provide the

Cheng et al.; Vision 2025: How To Succeed in the Global Chemistry Enterprise
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

practical route to the bulk synthesis of the elusive fullerenes and their derivatives, and provide new insights into the mechanism of fullerene formation.

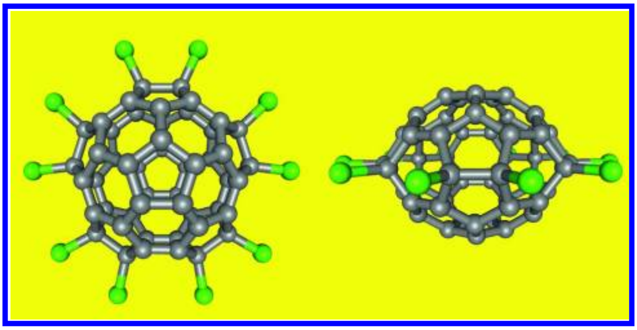


Figure 5. Schematic structure of $C_{50}Cl_{10}$. (see color insert)

Prof. Shi Gang Sun of Xiamen University in collaboration with Prof. Zhong Lin Wang of the Georgia Institute of Technology, USA, has used electrochemical synthesis to create a highly efficient new class of multifaceted catalysts, *i.e.* platinum nanocrystal catalysts with 24 facets, a breakthrough in the synthesis of nanoscale catalysts (*10*). These tetrahexahedral nanoparticles have high-index facets with unsaturated surface areas that help make the catalysts up to 4.3 times more efficient than spherical platinum nanoparticles (per unit platinum surface area) at oxidizing organic fuels such as formic acid and ethanol (Figure 6). In addition, the nanoparticles are remarkably robust and can remain stable at temperatures up to 800 °C, which makes them recyclable in relevant applications.

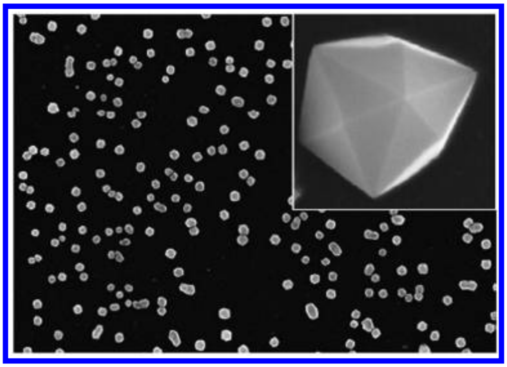


Figure 6. STM image of tetrahexahedral Pt nanocrystals (10).

2. Progresses in Advanced Materials Research

The theoretical research on the structural chemistry at Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences provided applicable guidelines to the discovery of new functional materials for optical applications, which posed a successful story of rational design of nonlinear optical (NLO) crystals. Theoretical studies on the relationship between crystal

Cheng et al.; Vision 2025: How To Succeed in the Global Chemistry Enterprise
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

structure and the NLO properties have directly led the way for the discovery of β-BaB_2O_4 (BBO) and LiB_3O_5 (LBO) (Figure 7). These achievements have paved the way for frequency conversion in both visible and UV regions. Large sized crystals with high optical quality are now available, thanks to the improvement of crystal growth technology. BBO and LBO crystals have become the major operating materials in today's solid state laser systems, and the mainstream in commercial opto-electronic products in both civil and military applications. The example shows a very successful case of transforming highly original research in fundamental chemistry to wide applications.

Figure 7. Large-sized nonlinear optical LBO crystals.

Organic solids are pi-conjugated functional molecules and polymers, charge transfer salts, and their nanostructures. They possess great potential in applications covering but not limited to display and lighting, field-effect transistors and printable electronics, solar energy conversions, bio- and chemical-sensing, information switching and storages, and anti-corrosion coatings, to name a few. Since 1980's Prof. Daoben Zhu from the Institute of Chemistry of the Chinese Academy of Sciences has successfully established a center of excellence in this field, namely, the Key Laboratory of Organic Solids. This laboratory, consisting of 14 independent research groups now, has gradually become a global elite research center in organic solids. Each year, more than 30 publications in the top chemistry journals such as *J. Am. Chem. Soc., Angew. Chem. Int. Ed., Adv. Mater* are produced from this laboratory. Zhu's laboratory is among the best in the world in organic semiconductor synthesis and device fabrication in the field of organic thin film transistors, organic light emitting diodes, organic solar cells, chemical- and bio-sensors, organic photonics crystals, as well as in bio-inspired interfacial materials. Recent advances include: (i) preparation of a number of novel organic semiconductors with mobility ~ 10 cm^2/Vs, including first demonstration of conjugated polymers with unprecedented high mobility of 8.2 cm^2/Vs and donor-acceptor alternatively co-crystalization which enable ambipolar and air-stable transports (*11*, *12*). The miniaturization has been realized with nanocrystal organic devices (Figure 8) (*13*); (ii) Light-emitting polymers containing either cations or anions in the side chains were employed as biosensors to detect the conformational change of DNA, enzyme activity, and more biomolecules (*14*, *15*). (iii) Novel n-type polymers and fullerene derivatives (ICBA) have been synthesized for better performance of organic solar cells (*16*).

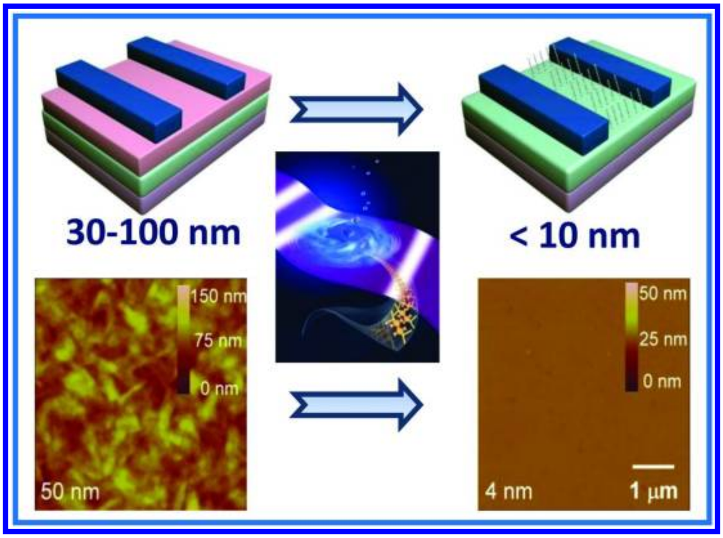


Figure 8. Organic electronic device can be made ultrathin at nanoscale. (see color insert)

Prof. Yong Cao group in South China University of Technology simplified polymer light-emitting diodes fabrication process by printing Ag-conducting paste on cationic conjugated polyelectrolyte surfcae as a bilayer cathode. This printing technology makes it possible to fabricate polymer light emitting device and displays without the use of thermal deposition, thus creating an avenue to achieve all printable roll-to-roll polymer light emitting devices and displays. When amino alkyl functionalized polyfluorene polyelectrolyte (PFN) is layered on RGB electroluminescent (EL) polymers, mixing does not occur since EL polymers are not soluble in methanol. Cao's group found that cationic water-/alcohol-soluble polyelecrolytes and their precursors allow efficient electron injection from high work function metals such as Al , Ag, and Au. Ag-paste cathode can also be printed on the top of PFN layer and the resultant PLEDs showed (device efficiency and EL spectra) comparable device performance to those with Ba, Ca and PFN/Ag (by thermal deposition) cathodes. The best luminous efficiency reached 7.8 and 5.6 cd/A for the green-emitting P-PPV and blue-emitting PFO devices with Ag-paste cathode, respectively. This is the first reported polymer light-emitting devices fabricated exclusively by printing technology without thermal deposition involved and a big step forward to make all printable roll-to-roll polymer light-emitting devices, displays and illumination sources (*17*, *18*). Their recent advance includes the invention of inverted structure for polymer solar cells; with their D-A copolymer blended with PCBM, power conversion efficiency reached a record high of 9.2% (*19*).

3. Advances in Molecular and Supramolecular Self-Assembly

Besides the wide panel of physical properties provided by functional compounds, organic nanostructures also exhibit a wide range of optical and electronic properties that depend sensitively on both their shapes and sizes. Prof. Jiannian Yao and coworkers in the Institute of Chemistry of the Chinese Academy of Sciences demonstrated the excellent features of organic nanostructures in lasing, waveguiding, multiple emissions and color tenability. Once integrated into a functional device, organic nanostructures should have a bright future. Although the tailor-made molecules can generally be obtained by organic synthesis, generating molecular aggregates with a specific structure and nanostructures with a desirable function remains a great challenge. Yao, et al. focused on the rational fabrication of organic nanostructures with a controllable shape, size, and therefore function. Aiming at a general strategy for creating well-defined supramolecular objects, they revealed how the molecular structures of building blocks affect the morphology of nanodimensional assemblies, and developed a kinetic control method for preparing 0D and 1D organic nanoheterojunction structures (Figure 9). Constructing highly-ordered superstructures through self-organization of organic nanostructures opens new routes to organic optoelectronic devices in a cost effective way (*20*, *21*).

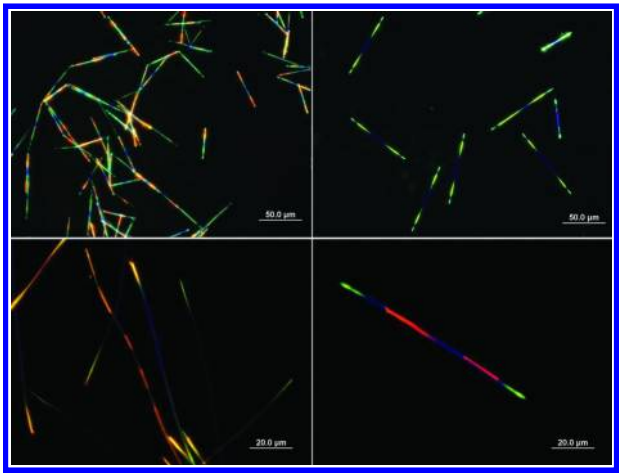


Figure 9. Yao et al. prepared organic nanoheterojucntions for optoelectronics application through molecular self-assembly. (see color insert)

Prof. Dongyuan Zhao of Fudan University in Shanghai has, *via* EISA strategy, created a series of highly ordered mesoporous polymers and carbons with 2-D hexagonal and 3-D cubic structures (*22*). The precursor is phenolic resol and the template is a mixed amphiphilic surfactant system of PEO-PPO-PEO and PPO-PEO-PPO. The mixed block copolymers interact with resols and assemble into cross-linked micelles that are suitable templates for constructing mesostructures. The interface curvature of the cross-linked micelle depends on the chemical composition, hydrophilicity/hydrophobicity as well as the specific feature of the reverse PPO-PEO-PPO (Figure 10).

Cheng et al.; Vision 2025: How To Succeed in the Global Chemistry Enterprise
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

Hyperbranched polymers (HBPs) are a new type of macromolecules with spherical and highly branched topology and a large population of terminal functional groups. Prof. Deyue Yan and co-workers of Shanghai Jiaotong University have prepared many types of HBPs self-assemblies at all scales and dimensions (Figure 12) (*23*, *24*). These self-assemblies can be macroscopic tubes, physical gels, micro- or nano-vesicles, fibers, spherical micelles, honeycomb films and large compound vesicles, depending on the media in which they formed. In addition, Yan's group have found that the vesicles self-assembled from HBPs possess good membrane fluidity like liposomes and strong stability like polymersomes, serving as a simple model membrane to mimic cellular morphologies and functions. Indeed, they have observed membrane fusion, fission, swelling, and shrinkage by using the polymer vesicles self-assembled from a hyperbranched polyether (Figure 11). These findings help lead to the discovery of new supramolecular structures as well as the new applications, and shed lights on the underlying principle of self-assembly in nature.

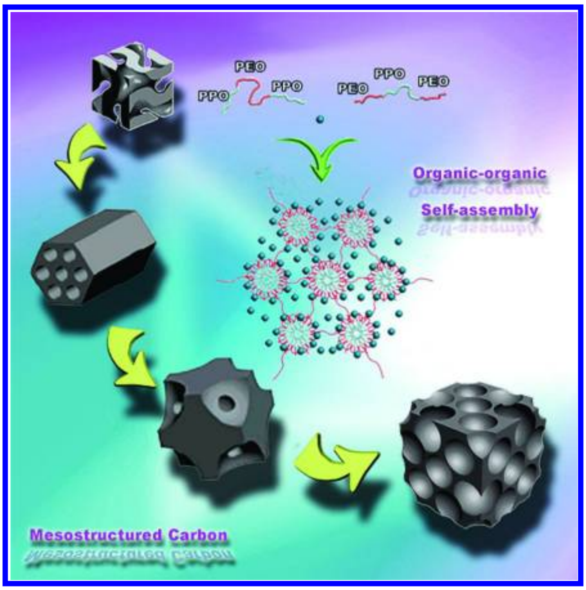


Figure 10. Mesostructured carbon. (see color insert)

The development of new building blocks and creation of diversified supramolecular nanostructures have always been the most important parts in the area of self-assembly. In contrast to conventional amphiphiles based on covalent bonds, Prof. Xi Zhang of Tsinghua University developed a new field of supra-amphiphiles that refer to amphiphiles constructed on the basis of noncovalent interactions or dynamic covalent bonds (*25–27*). In supra-amphiphiles, functional moieties can be attached by noncovalent synthesis, greatly reducing the need for tedious chemical synthesis (Figure 12). The building blocks for supra-amphiphiles can be either small molecules or polymers. The advance of supra-amphiphiles will not only enrich the family of

Cheng et al.; Vision 2025: How To Succeed in the Global Chemistry Enterprise
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

conventional amphiphiles but also provide a new kind of building blocks toward complex self-assemblies, including hierarchical self-assemblies and functional nanostructures.

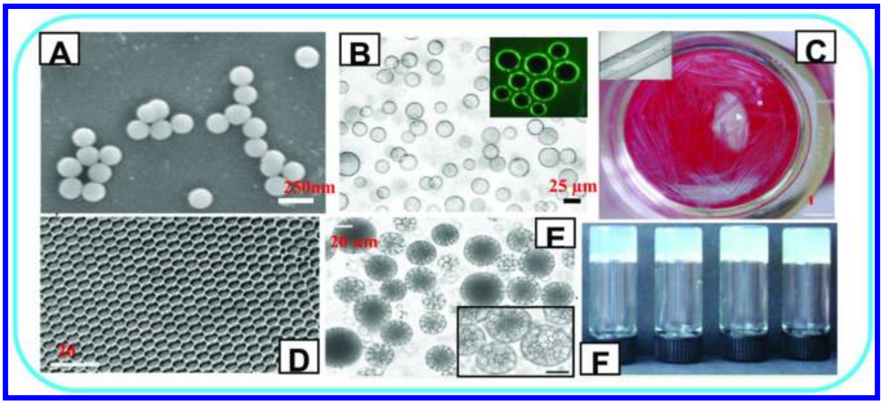


Figure 11. Self-assembly of hyperbranched polymers. (A) spherical micelles; (B) giant vesicles; (C) macroscopic multiwalled tubes; (D) honeycomb-patterned films; (E) large compound vesicles; (F) physical gels. (see color insert)

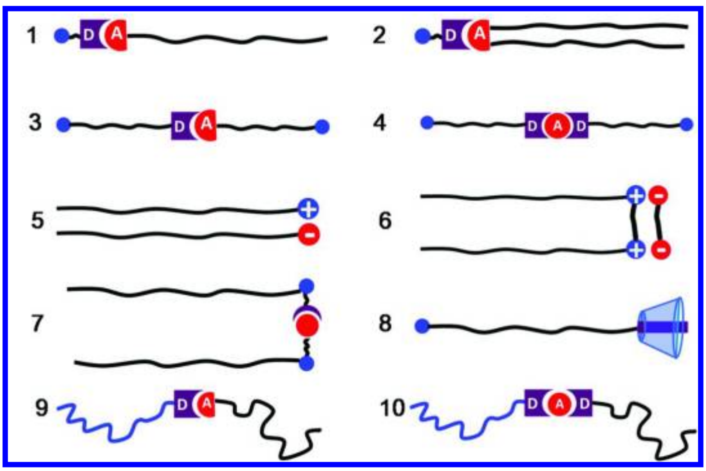
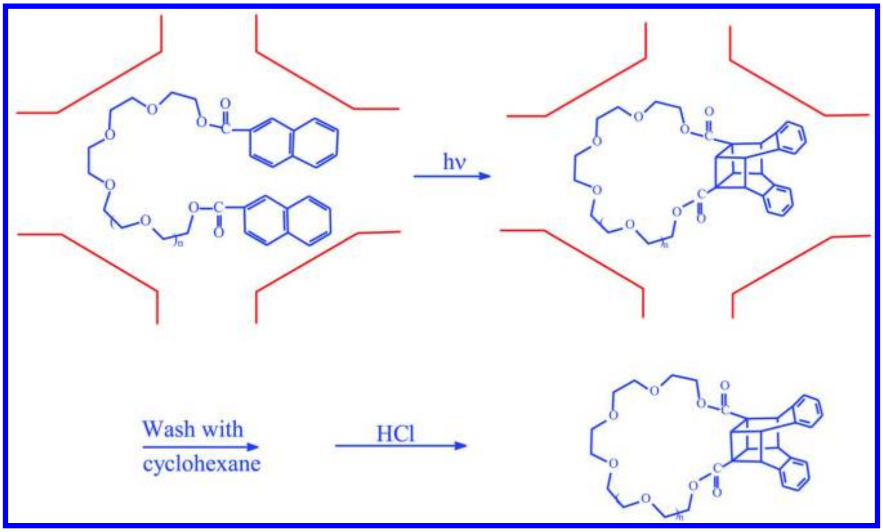


Figure 12. Molecular Engineering of supra-amphiphiles.

4. Advances in Organic Synthesis

The efficient and highly selective synthetic method is always one of the holy grails in chemistry. Profs. Chen-Ho Tung, Lizhu Wu and their co-workers utilized molecular aggregates, cavities and surfaces of microporous solids as microreactors to successfully control the product selectivity in organic photochemical reactions. They devised a new procedure for the preparation of large-ring compounds with high yields under high substrate concentrations by using microreactors (Scheme

2). They could direct the photosensitized oxidation of alkenes selectively towards either the singlet oxygen mediated or the superoxide radical anion mediated products by controlling the status, the location of the substrate and the sensitizer molecules in the microreactor. A number of products that are difficult to prepared in homogeneous solutions are easily synthesized using this mathod (*28–30*).



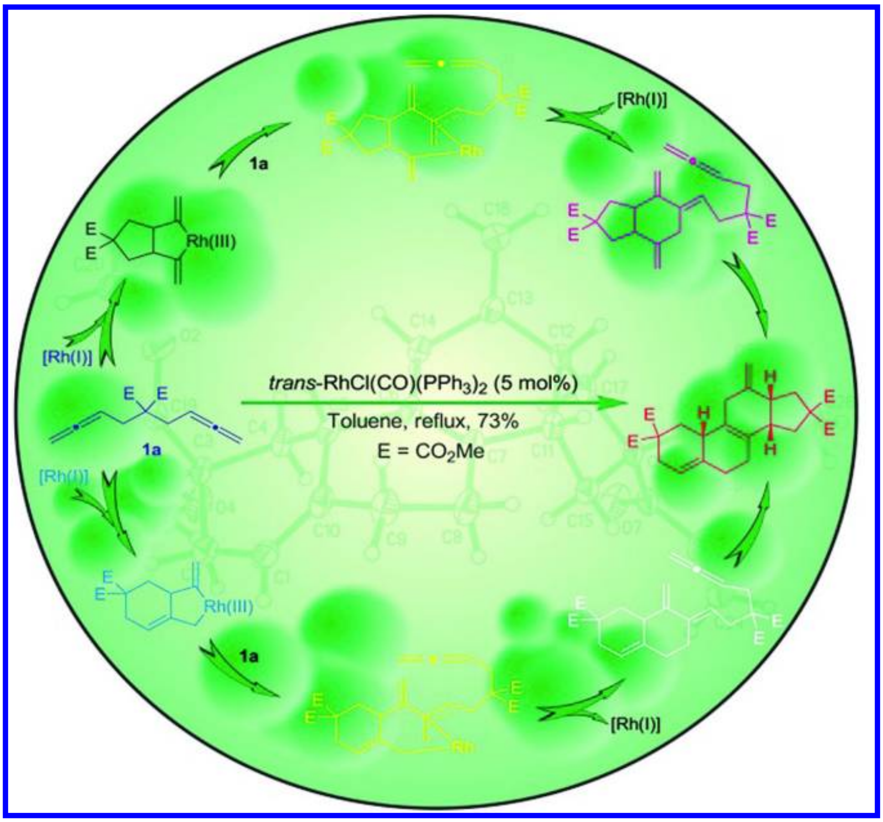
Scheme 2. Micro-reactor for photochemistry synthesis. (see color insert)

Allenes are a class of compounds with interesting reactivity due to their unique structures. They were considered to be “highly unstable” for a long period of time. Prof. Shengming Ma’s group has played a major role in allene chemistry, discovering the cyclization of functionalized allenes and the addition reactions of allenes. They found that the two- or three-component reactions can very efficiently produce poly-substituted butenolides, vinylic epoxides, 2,5-dihydrofurans, furans among many others. His group has demonstrated that 1,5-bisallenes can undergo cyclometalation in one step to form complicated skeletons including the steroid-like derivatives with highly stereoselectivity. Nucleophilic conjugate addition reactions of 1,2-allenyl carboxylic acids, esters, amides, and ketones have been developed for the high regio- and stereo-selective synthesis of functionalized alkenes, which are usually difficult to obtain due to the potential migration of the C=C bond. His group has also developed the halo- or seleno-hydroxylation of 1,2-allenyl sulfides, selenides, sulfoxides, sulfones, phosphonates, phosphine oxides, beta-(1,2-allenyl)butenolides, with very high regio- and stereoselectivity. These contributions render allenes very useful in organic synthesis (Scheme 3).

Transition metal-catalyzed asymmetric catalysis is one of the most powerful methods for producing optically active chiral building blocks used in the synthesis of natural products, chiral drugs, agrochemicals, and chiral materials

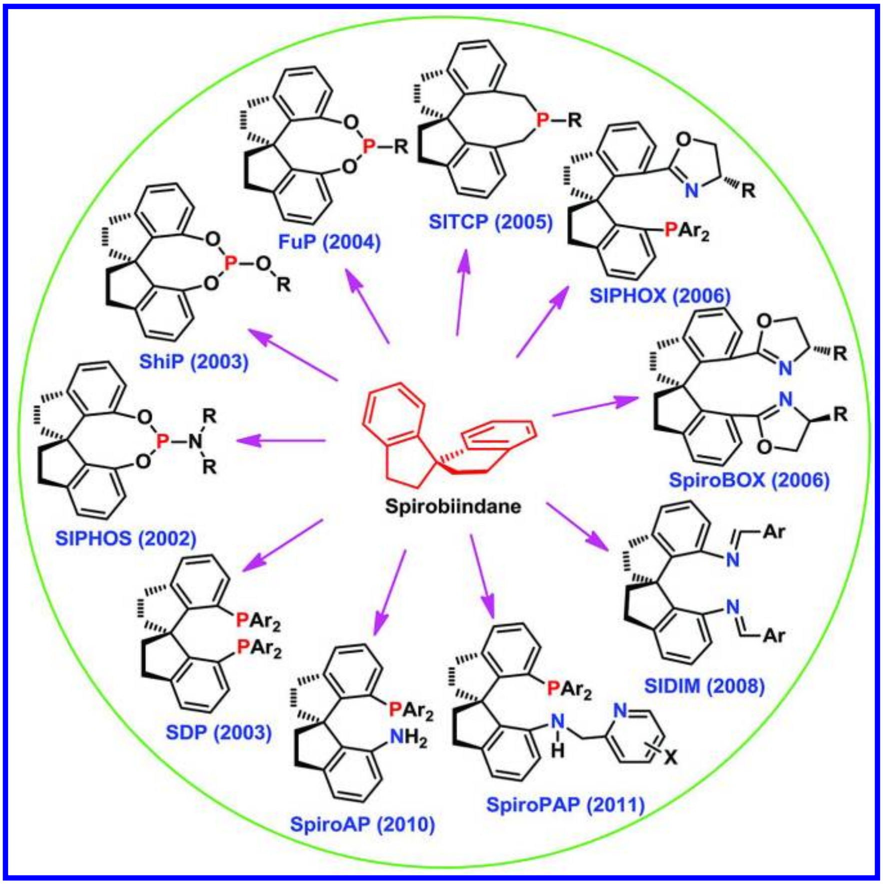
Cheng et al.; Vision 2025: How To Succeed in the Global Chemistry Enterprise
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

in an environment-friendly and sustainable manner. In the study of transition metal-catalyzed asymmetric catalysis, the design and synthesis of efficient chiral ligands and catalysts is the central goal. Since the beginning of this century, Prof. Qilin Zhou at Nankai University developed a new type of chiral ligands based on the novel 1,1′-spirobiindane backbone including diphosphines SDPs, bisoxazolines SpiroBOXs, phosphine-oxazolines SIPHOXs, a wide range of monodentate phosphorous ligands such as SIPHOS and others (*31–35*). These spirobiindane ligands and the corresponding catalysts possess the advantages of high rigidity and stability, perfect C2-symmetry, as well as easy modification. The chiral spiro ligands and catalysts have been demonstrated to be highly efficient and enantioselective for many asymmetric reactions such as asymmetric hydrogenations of enamines, imines, unsaturated carboxylic acids, and simple ketones, asymmetric insertions of carbenes into heteroatom–hydrogen bonds (X−H; X = O, N, S, Si), and asymmetric carbon-carbon bond-forming reactions, see Scheme 4. These chiral spiro ligands and catalysts have been accepted as a privileged group of chiral ligands and catalysts, and this work is considered an extraordinary contribution to chiral science and technology.



Scheme 3. Allenes chemistry.

Cheng et al.; Vision 2025: How To Succeed in the Global Chemistry Enterprise
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

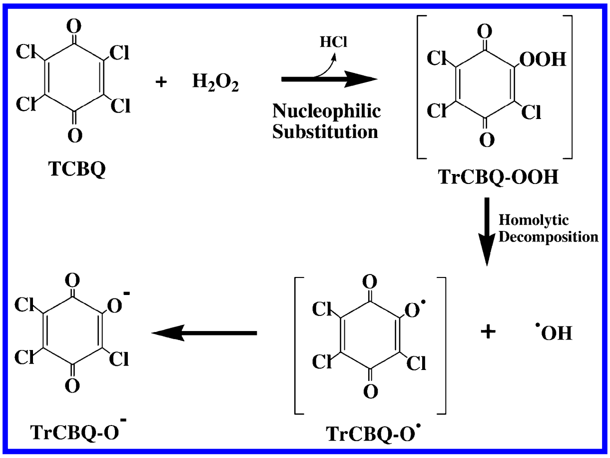


Scheme 4. Example of chiral spiro ligands.

5. Advances in Environmental Chemistry

It has been previously shown that hydroxyl radicals (HO•) can be produced by H_2O_2 and halogenated quinones, independent of transition metal ions. However, the underlying molecular mechanism is still unclear. Prof. Gui-Bin Jiang and coworkers from the Research Center for Eco-Environmental Sciences of the Chinese Academy of Sciences, found that it is tetrachloro-1,4-benzoquinone (TCBQ), instead of its corresponding semiquinone anion radical, the tetrachlorosemiquinone anion radical ($TCSQ^{\bullet -}$), that is essentially responsible for $HO^{\bullet}$ production. They propose a novel mechanism: a nucleophilic attack of H_2O_2 onto TCBQ, forming a trichloro-hydroperoxyl-1,4-benzoquinone (TrCBQ-OOH) intermediate, which decomposes homolytically to produce $HO^{\bullet}$, see Scheme 5. It has also been found that the halogenated quinones could enhance the decomposition of organic hydroperoxides and formation of alkoxyl radicals in a similar pathway. These findings may explain the carcinogenicity of the widely used biocides including polychlorinated phenols (such as wood preservatives pentachlorophenol, 2,4,6- and 2,4,5-trichlorophenol), hexachlorobenzene, and

Agent Orange (the mixture of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2,4-dichlorophenoxyacetic acid (2,4-D)), because these compounds can be metabolized *in vivo* to tetra-, di- or mono-chlorinated quinones (*36*, *37*).



Scheme 5. Proposed mechanism of HO radical production by TCBQ and H_2O_2 (37).

To promote efficient use of solar energy, many efforts have been devoted to the modification of TiO_2 to extend its spectral response to visible region. A group led by Prof. Jincai Zhao in the Institute of Chemistry of the Chinese Academy of Sciences has successfully improved the photocatalytic activity in the visible region. Through doping the nonmetal element boron and the metal oxide Ni_2O_3 in TiO_2, toxic organic pollutants such as trichlorophenol (TCP), 2,4-dichlorophenol (24-DCP) and sodium benzoate can be efficiently degraded and mineralized. A density functional theory calculation by Prof. Zhigang Shuai showed that boron doping can induce mid-gap band, thus extending the absorption range. The dechlorination and mineralization results point towards the photocatalytic pathway via visible light excitation (*38*).

6. Advances in Fundamental Physical and Theoretical Chemistry

Physical and theoretical chemistry is the foundation of chemical sciences. Resonances in the transition state region are important in many chemical reactions near the reaction energy thresholds. Detecting and characterizing isolated reaction resonances, however, have been a major challenge in both experiment and theory. A research group led by Profs. Xueming Yang and Dong Hui Zhang from Dalian Institute of Chemical Physics of the Chinese Academy of Sciences has carried out a series of high resolution crossed-molecular-beams scattering experiments on the F+H_2/HD reaction with product quantum states fully resolved (*39*), in combination with quantum dynamics calculations on accurate potential energy surfaces. Pronounced forward scattering for the HF(v′=2) product has been observed at the collision energy of 0.52 kcal/mol in the F+H_2(j=0) reaction (Figure 13). Quantum dynamical calculations based on new potential energy surfaces show that the forward scattering of HF(v′=2) is due to two Feshbach resonances. Quantum state resolved scattering on the isotope substituted F+HD→HF+D reaction has been studied. A remarkable, fast changing dynamical picture has been observed, providing an extremely sensitive probe to study the resonance picture of this benchmark system. Furthermore, forward scattering HF(v′=3) product from the F+H_2 reaction was also observed and attributed mainly to a slow-down mechanism over the centrifugal exit barrier. More interestingly, based on the theoretical prediction made on an accurate potential energy surface, the group observed a clear oscillatory structure assigned to J = 12 to 14 partial waves in the collision energy dependence of the state and angle-resolved differential cross sections (Figure 14) (*40*). From these concerted experimental and theoretical studies, a clear physical picture of the reaction resonances has emerged, providing a textbook example of dynamical resonances in elementary chemical reactions.

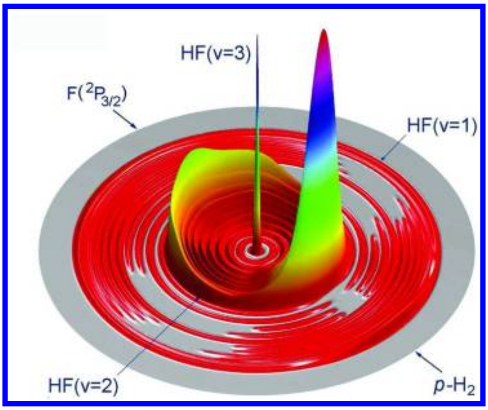


Figure 13. The 3D contour plot of the experimental differential cross sections for the F+H2 reaction at the collision energy of 0.52 kcal/mol.

Surface-enhanced Raman scattering (SERS) is a powerful spectroscopy technique that can provide non-destructive and ultrasensitive characterization down to single molecular level, comparable to single-molecule fluorescence spectroscopy. However, general substrates based on metals such as Ag, Au and Cu, either with roughened surfaces or in the form of nanoparticles, are required to realize a substantial SERS effect, and this has severely limited the breadth of practical applications of SERS. Tian group in Xiamen University report an approach, named shell-isolated nanoparticle-enhanced Raman spectroscopy, in which the Raman signal amplification is provided by gold nanoparticles with an ultrathin silica or alumina shell. A monolayer of such nanoparticles is spread as ‘smart dust’ over the surface that is to be probed. The ultrathin coating keeps the nanoparticles from agglomerating, separates them from direct contact with the probed material and allows the nanoparticles to conform to different contours of substrates. They have been able to obtain high-quality Raman signal from various species on a broad range of samples, including single crystal metal and semiconductor surfaces, fruits, living cells. SHINERS method has significantly expanded the flexibility of SERS for useful applications in materials and life sciences, as well as for the inspection of food safety, drugs, explosives and environmental pollutants. By placing a sharp Au or Ag tip with high surface plasmonic resonance quality close to a sample surface, the Raman signal of the sample can also be significantly enhanced right in the vicinity of the tip. This method provides high spatial resolution and high sensitivity (Figure 15). They also developed a method called fishing mode tip-enhanced Raman spectroscopy, to significantly increase the chance to form tip-molecule-substrate junction, and to allow mutually verifiable single-molecule conductance and Raman signals with single-molecule contributions to be acquired simultaneously at room temperature. In particular, they revealed that a stronger bonding interaction between the molecule and tip may account for the nonlinear dependence of conductance on bias voltage. FM-TERS will lead to a better understanding of electron-transport processes in molecular junctions (*41*, *42*).

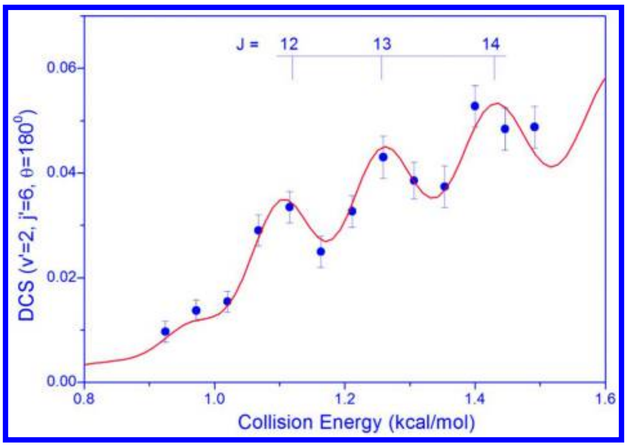


Figure 14. Experimental and theoretical DCS of the HF(v'= 2, j'= 6)product of the F($^2P_{3/2}$) + HD(j = 0) reaction in the backward scattering direction. The solid circles are experimental data; the red curve, the result of full quantum dynamics calculations convoluted with the experimental resolution and shifted 0.03 kcal/mol lower in energy. (see color insert)

Song Gao of Peking University has discovered novel magnetic relaxation phenomena in single-chain magnet and single-ion magnet. By choosing metal ions with large magnetic anisotropy, and by employing azido to transfer magnetic interaction and proper terminal ligands to isolate the individual magnetic chains so as to satisfy Glauber's dynamic conditions, his group has successfully obtained the first examples of homo-spin single-chain magnet (*43*), see Figure 16). Using diamagnetic ions and/or long bridging ligands to separate the paramagnetic ions efficiently, his group has found that some weakly coupled systems exhibit the external field-dependent magnetic relaxation phenomena, which are quite similar to, but different from, the relaxation in superparamagnets . He also discovered a series of novel molecular magnets based on cyanide (CN−), azide (N3−), dicyanide (C(CN)2−), cyanamide (NCNH−) and formate (HCOO−). In particular, he and his collaborators have synthesized some new hetero-metallic (3d-4f, 3d-3d′, 3d-4d) magnets, mixed-bridged hybrid magnets, weak ferromagnets constructed by asymmetric three-atom single bridges and porous magnets (*44*). These discoveries are of great importance in understanding the quantum origin of molecular magnetism.

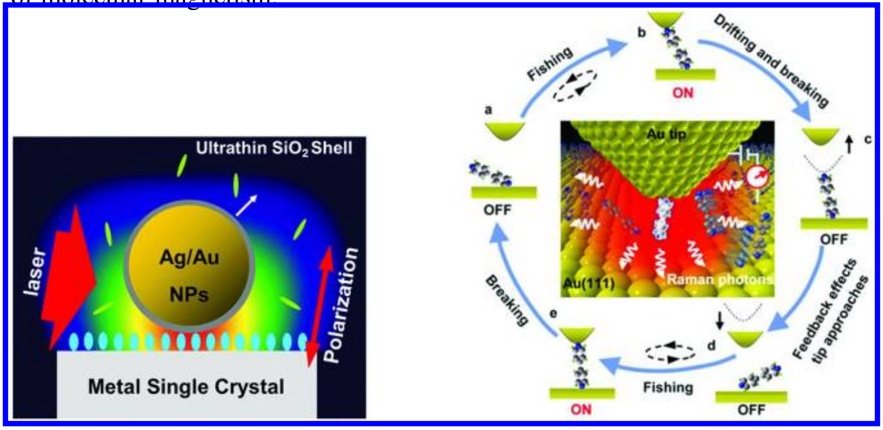


Figure 15. Left: The Principle of shell-isolated nanoparticle-enhanced Raman spectroscopy to obtain surface Raman signal on surfaces or species that do not support enhancement. Right: A schematic diagram of fishing-mode tip-enhanced Raman spectroscopy that allows the Raman and electric conductance signals of single molecules to be obtained simultaneously. (see color insert)

Prof. Wenjian Liu from Peking University developed a method to eliminate symmetrically the small component of the wavefunction in relativistic quantum chemistry, resulting in a new Hamiltonian, that is easily solved. His approach is conceptually simple, numerically accurate, computationally efficient and serves as a seamless bridge between Dirac and Schrödinger equations (*45*). Another contribution of Prof. Wenjian Liu is the novel formulation of relativistic theory for the determination of nuclear magnetic resonance (NMR) parameters. In addition, he has explored the first time-dependent relativistic density functional theory for electronic excitations in heavy atoms. These developments have rendered the BDF (Beijing Density Functional, of which Liu is an important developer) package very powerful in first-principles electronic structure calculations for heavy atoms.

Prof. Shuhua Li in Nanjing University has developed an efficient linear scaling method for computing the electronic structures of large molecules. One of the strategies adopted is the cluster-in-molecule (CIM) local correlation technique, which can extend the applications of *ab initio* correlation methods (CCSD or MP2) to large molecules (*46*, *47*). The CIM approach is based on the "locality" of electron correlation, and is considered to be one of the representative linear scaling coupled cluster algorithms. Another strategy is the energy-based fragmentation approach. In this scheme, the total energy of a large molecule can be calculated approximately from energy calculations on a small subsystem. This method has been applied to various biological molecules or molecular clusters at various theoretical levels. It has been used for the calculation of the ground-state energies and structure optimization, vibrational spectra, and some molecular properties at *ab initio* levels for more than 1000 heavy atoms, which are well beyond the reach of traditional computational methods.

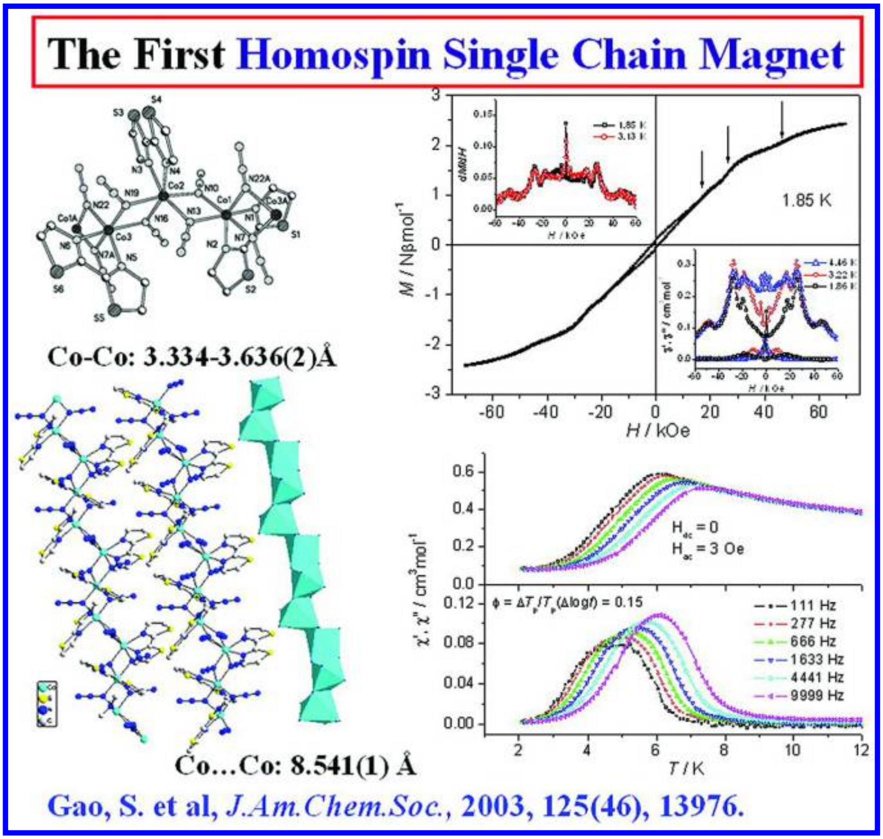


Figure 16. The first homospin single chain magnet. Reproduced with permission from reference (43). Copyright 2003 American Chemical Society. (see color insert)

It is widely noted that excited state is at the center of interest for theoretical chemistry, both from the electronic structure and from the chemical dynamics perspectives. For complex system, time dependent density functional theory (TDDFT) nowadays becomes the standard computational tool to reveal the electronic excited state structures. Energy gradient is pivotal both for geometry optimization, response theory, as well as property evaluation. While algorithm for the first-order analytical gradient for the excited state in the framework of TDDFT has been obtained a while ago, the second-order gradient has not been available for long time. People rely on numerical evaluation that is both time-consuming and inaccurate. Prof. Wanzhen Liang from Xiamen University has recently been successful in achieving an analytical solution for the second-order gradient with respect to both atomic coordinates and external field. This is a breakthrough in TDDFT with wide application both for excited state structure and chemical dynamics calculations (*48*, *49*).

Theoretical chemistry is popularly classified into three domains: structure theory, chemical dynamics, and statistical mechanics. Prof. Zhigang Shuai aims at developing reliable theoretical methods for the prediction of the properties of materials, which requires a trio of the three instead of a solo. The first example is his recent work on quantitative prediction of quantum efficiency of molecular fluorescence. Prof. Zhigang Shuai and Jiushu Shao have recently developed a new analytical formalism for determining the nonradiative decay rate constants by taking into account multimode mixing due to Duschinsky rotation for potential energy surfaces of the excited and the ground states (*50*). The theory successfully demonstrates completely different photophysical behaviors for the two isomers of tetraphenylbutadienes, thus providing a reasonable explanation of the aggregation induced emission phenomena for one isomer. This allows an "*ab initio*" molecular fluorescence efficiency prediction (*51*). Shuai *et al.* further employed hybrid quantum mechanics/molecular mechanics (QM/MM) approach to investigate the excited state decay in molecular aggregate (Figure 17). In contrast to the conventional aggregation quenching, some luminophors can exhibit exotic aggregation induced emission phenomena. From Shuai' calculations, it is found that the intermolecular electrostatic interaction could suppress low-frequency motion to reduce the non-radiative decay and to enhance the luminescence quantum efficiency. To predict the charge mobility in optoelectronic materials, Shuai *et al.* have developed a first-principles scheme based on hopping mechanism by combining quantum chemical calculations plus a statistical simulation (Random Walk) to investigate charge transports. He showed that (i) the quantum nuclear tunneling effect is essential, and (ii) the dynamic disorder does not play an appreciable role for charge hopping transport in organic semiconductors. Later, his model was not only found to be able to explain the apparently "paradoxical" experimental observations that optical measurement indicated "localized charge" while electrical measurement indicated "bandlike," but also directly got several experimental verifications (*52*, *53*). Such nuclear tunneling model was even adopted to conducting polymers for clarifying the recent dispute over the charge transport mechanism.

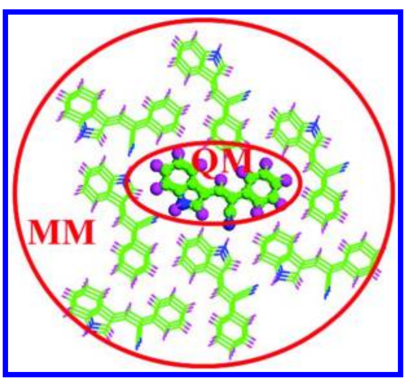


Figure 17. Shuai developed a QM/MM method for studying the quantum efficiency of the organic light-emitting materials.

Sharing International Responsibilities

Chinese chemists are becoming more and more active in the international arena, not only because they are becoming known internationally, but also because they are sharing more and more international responsibilities. We are facing serious global challenges such as environment and natural resources. These are the problems to be solved through chemistry R&D, and international collaborations are indispensable. Under such circumstances, national chemical societies along with corresponding funding agencies from China, US, Japan, Germany and UK have decided to launch a yearly summit to discuss the urgent issues addressing global challenges in energy, environment, resources and water, health and nutrition, and global warming. In 2008, the representatives from the five countries formed a steering committee for the summit, named “Chemical Sciences and Society Symposium (CS3)” and later changed to “Chemical Sciences and Society Summit (CS3)”. The purpose is to unite the talent of international chemists to identify the essential challenges in chemistry in order to provide a roadmap to solve these global problems.

The first CS3 took place in Kloster Seeon, Germany, 2009, which was organized by the German Chemical Society, focusing on the subject of “Using Sunlight to Power the World”. The major suggestions are shown below:

(i) *Converting solar energy into chemical fuel through artificial photosynthesis mimicking natural processes*. Chemists should develop chemical catalysts for water splitting and CO_2 reduction that can be applied commercially and are made of affordable and earth-abundant materials. Chemists also must create an “artificial leaf” by coupling water splitting and CO_2 reduction in a way that eliminates the need for an external and sacrificial electron donor.

(ii) *Accessing solar energy that already exists in nature.* Chemists must develop biochemical methods that can be used to create more biomass and develop catalytic processes that improve the efficiency of biomass conversion.

(iii) *Converting solar energy into electricity.* Since the widespread use of silicon-based photovoltaic cells is limited due to high cost, chemists must develop low-cost, non-toxic, earth-abundant photovoltaic materials for use in next generation photovoltaic cells.

(iv) *Storing newly harnessed and converted solar energy.* Chemists must develop new catalysts and materials from low-cost, earth-abundant elements that can be used to build affordable, sustainable solar energy transformation and storage systems.

The second CS3 took place in London, organized by the Royal Society of Chemistry in 2010. It focused on the various facets of “Sustainable Materials”. It was suggested that materials chemists

(i) must develop new, sustainable energy conversion and storage technologies that can meet the future energy demands, and without increasing harmful emissions of CO_2.
(ii) can help to reduce CO_2 emissions by improving carbon capture and storage systems and developing novel ways of activating and using CO_2 as a value product for fuels and chemical feedstocks rather than waste.
(iii) must develop methods to efficiently obtain petroleum from low-quality sources and processes to efficiently and sustainably utilize fossil fuel alternatives to reduce our dependency on fossil fuel and feedstocks.
(iv) must reduce, replace and recycle the use of scarce natural resources in many applications, as well as developing alternative new materials based on earth-abundant elements.
(v) must use the principles of green chemistry to meet our energy, materials and water needs in ways that are non-harmful and sustainable. New technologies can be developed to better monitor and remove air, soil, and water pollutants from the environment.

The third “CS3” took place in Beijing and was organized by the Chinese Chemical Society in 2011. The summit focused on the theme of “Health”. Deadly infectious diseases have been conquered in most regions of the world, but they remain as constant threats. The non-infectious diseases, often chronic, become major concerns. Examples are cardiovascular disease and cancer, which are now the main causes of death. It was recommended that:

(i) Chemists should better understand the chemistry of infection and non-infectious diseases as well as the immune system. They must study the role of reactive oxygen species in age-related diseases through the investigation of brain chemistry and aging processes. Accordingly, novel tools should be developed for studying the life processes.
(ii) Chemists play an essential role in drug design. They should better understand the interaction between drug molecules and biological molecules and develop more sensitive methods for monitoring the interactions between individual molecules in a cell. Chemists must develop better ways to screen natural products and develop new antibiotics and find ways to make drug manufacturing cheaper, more efficient, less wasteful and less reliant on petroleum.
(iii) Chemists must develop better tools for validating and studying biomarkers as well as for detecting individual molecules in cells. They must develop better imaging technologies at a wide range of scales and low-cost genome sequencing technologies.

The fourth “CS3” took place in San Francisco, 2012, organized by the American Chemical Society, focusing on organic and carbon electronics. It was noted that organic electronic devices will do things that silicon-based electronics cannot do, expanding the functionality and accessibility of electronics and will be more energy-efficient and eco-friendly. The following strategies have been recommended:

(i) improving controlled self-assembly. Chemists need to gain better control over the self-assembly of organic electronic molecules into ordered patterns to ensure that the structures being assembled are reproducible, which requires a better understanding of the interfacial behaviors.
(ii) improving three-dimensional processing technology. Chemists must develop processes to fabricate three-dimensional organic electronic structures with the same precision achievable nowadays with two-dimensional printing technology for reliable high-throughput manufacturing of organic electronic devices.
(iii) increasing multi-functionality of organic electronic devices. As chemists gain better control over the synthesis of organic materials, they will be able to build increasingly sophisticated optoelectronic and other devices. Chemists need to broaden their research focus beyond charge carrier transport and gain better understanding of optical, magnetic, thermal and other properties.
(iv) developing better analytical tools. Chemists need better tools for analyzing the molecular composition, molecular organization, and local electronic and other properties of the organic electronic systems.

Chinese Chemical Society (CCS) is a national adhering organization of the International Union of Pure and Applied Chemistry (IUPAC) since 1979 and is also an active member of the Federation of Asian Chemical Societies (FACS). CCS has officially established close cooperation relationships with several national chemical societies, including the Royal Society of Chemistry (RSC), the German Chemical Society (GDCh), the American Chemical Society (ACS), and the Chemical Society of Japan (CSJ). In 2005, ACS sent a delegation with a large number of high profile leaders and chemists to visit CCS, Chinese Academy of Sciences, Ministry of Science and Technology, National Natural Science Foundation, as well as the several elite institutions in chemistry. Since then, CCS-ACS entered into a strategic alliance relationship. CCS-ACS alliance is committed to working together to create a better environment for chemistry to make a positive impact on our society. Every year, the Presidents from both societies issue a joint comment publicly to suggest chemistry solutions to one global issue, as well as to publicize the joint activities of both societies. These comments are published in both "C&E News" and "Chemistry Letters". CCS delegations have paid visits to the headquarters of RSC and GDCh in 2007 to strengthen the established ties. During the CCS Biennial Congress, the leaders from international chemical societies have been invited to come to China for official visits, during which bilateral symposia on mutually interested topic were organized.

Challenges and Opportunities for Chemistry in China

Chemical sciences will continue to be pivotal and indispensable in creating new matters and shaping the development of novel methodologies and new theories. The research frontiers lie in a huge arena ranging from single atoms, single molecules to molecular assemblies in a multiscale world, aiming at establishing the relationship between the properties or functions of these atomic buildups and their structures at different scales. While chemical sciences focus on the unified description at both microscopic and macroscopic levels, revealing the static and dynamic behaviors which will deepen our understandings of matters from simple to complicated perspectives and/or the other way around. The interdisciplinary research with physics, life sciences, materials sciences and information science is essential to solve important problems in environments, energy and resources. Chemical sciences will advance not only in the fundamental understanding of matter, its structure and properties, but also meet the needs of people for progress and prosperity.

Economy is and will still be booming in the foreseeable future in China. There are tremendous opportunities for scientists to carry out cutting-edge research in chemical sciences. Of the most importance includes the exploration of diversity of structures of matter and molecules, synthetic methodologies for creating small molecules, polymer, biomolecules, as well as rational design of the assembly of supramolecular systems, combinatorial, novel synthetic strategy. The structure and transformation of matter are always at the heart of chemistry. It is expected that elucidation of the multiscale structure of matter and investigation on the relationships between structures and properties and functions will be the mainframe of chemical sciences. These structures here generally refer to molecular geometry, the chain conformations of polymers, the folding state, configuration of the supramolecular assembly, higher level structure of biomolecules and formation of nanostructures. The following areas are full of opportunities and challenges.

1. Novel Synthetic Strategies, Concepts, and Methods

As the major means of creating new substances, the methodologies and strategies of inorganic, organic, polymer, solid and combinatorial syntheses lie in the core of chemical sciences. Research in this direction is highly target-oriented, requiring originality, creativity, and interdisciplinary interactions.

The key issue is to develop new synthetic methods, to design and to synthesize compounds of desired properties and new molecular systems, which cannot be realized by merely resorting to trial and error or by traditional procedures. A designing scheme based on structure, mechanism as well as the reaction dynamics should be rationalized. The ultimate goal of modern synthetic chemistry is to make a substance of specified structure and function with high efficiency and selectivity, meeting the needs of functionalized chemicals in life, material, information, energy and environmental sciences. Nowadays, the most active and exciting research frontiers include asymmetric organic synthesis and controllable formation of ordered structures. Novel ideas are required to achieve this goal. A breakthrough in this research will not only help understand the origin of biological homochirality, but also be invaluable in improving the techniques in pharmaceutical, agrichemical, and materials industry.

The advances in synthetic chemistry will also gain momentum from other academic disciplines such as biology, physics, material science, information sciences as well as environmental science. Synthetic strategies by virtue of biological and physical laws and effects can be anticipated to assist chemists to invent new routes for synthesis.

Major challenges include:

(a) Function oriented synthesis: methods and strategy
(b) Highly selective synthesis *a la* catalyzed asymmetric synthesis
(c) Molecular design and synthesis of specific structures and properties
(d) Synthesis and manufacture under mild and extreme conditions
(e) Activation and transformation of inert chemical bonds

2. Chemical Dynamics and Control: Experiments and Theories

Chemical dynamics experiments aim at observing and controlling the real-time evolution of chemical processes, while theories can predict the dynamic behavior and tell the optimal conditions for active control. The dynamics of typical elementary reactions, particularly those involving quantum effects including oscillation of wave packets, tunneling as well as interference can be further explored by experimental measurements and theoretical calculations. The recognition, reaction, and manipulation of single molecules will be a hot topic. The underlying basis of chemical bonding and interaction for single molecules is yet to be clarified. Novel methods in quantum chemistry and chemical dynamics will be developed for more accurate description of structures as well as dynamic processes. The focuses will be the energetics of transient intermediates, reaction pathways, and chemistry and physics of single molecules.

Major challenges include:

(a) Chemical dynamics: Theory and experimental techniques
(b) Understanding and control of ultrafast processes in chemical reactions
(c) Probe of structures and dynamic motion of single molecules on surfaces
(d) Investigation of mechanisms of catalytic reactions
(e) Dynamics and control of chemical reactions on interfaces

3. Molecular Assembly, Ordered Structure, and Function

The properties of matter depend not only on the structure of its building molecules, but to some extent also on the structure of the assemblies. For small molecules, the study on the formation of their crystals and nanostructures will be a fundamental one. For synthetic polymers, investigation on the structure and motion of the polymeric chain as well as diversified condensed states will be essential to design specific structures and new materials that possess desired properties. Once their ordered structures and chemistry of assembly are known, supramolecular systems or nonbonded assemblies can be constructed with inorganic and organic molecules, biomolecules, and polymers. For theorists, a methodology based on chemistry, life sciences, physics for assembly chemistry, full of explanatory and predictive power, is yet to be set up. The theory should include a good description of the nature of the weak intermolecular interaction, electron transfer, energy transfer, matter transport, and chemical transformations. With these, one can establish the relationship between the formation of molecular assembly with specific structure and ordered higher-level structure. Therefore, one can use theoretical findings to design basic units of desired properties and functions.

Major challenges include:

(a) Nature of the weak intermolecular interaction and position recognition
(b) Growth dynamics for molecular assembly and ordered higher structures
(c) Reactivity of relation-structure relationship of molecular assemblies
(d) Construction and functions of novel supramolecular systems

4. Theoretical and Computational Methods for Complex Chemical Systems

Chemical theory will play an increasingly important role in the development of chemical sciences in the 21st century. Future development will focus on the theoretical and computational approaches for complex chemical systems that are important in biology, materials, and environmental sciences. Inorganic solids, large organic and biomolecules, supramolecular systems, interfaces are all examples of complex systems. Not only the characteristics of the microscopic state or gas phase at zero temperature, but also the real property of molecular ensemble or thermal state should be calculated. Theoretical and computational chemistry is essentially an interdisciplinary research area on multi-scale phenomena in both space and time. As an indispensable part of chemistry, in either conceptual understanding or quantitative characterization, theoretical chemistry will continue to benefit from assimilation of state-of-the-art results of mathematics, physics, computer sciences, and other sciences.

Major challenges include:

(a) Computational chemistry
(b) Methodology of assessment of properties based on electronic structures
(c) Theoretical dynamics for micro, meso- and macromolecular systems
(d) Theoretical treatment for the chemical dynamics of interfaces, metastable systems and small systems

5. New Techniques and Approaches for Chemical Analysis and Detection

Analysis, detection, and characterization are the means of acquiring the information on chemical components, structures, and interactions in molecular systems. Advancement in chemical sciences heavily relies on the development of new principles and methodologies for analysis and detection, so do many other fields such as life, material, environments, energy, health and medical sciences, security, and economics. In fact, major advancements in scientific research can be attributed to the improvements in methodologies and tools. For example, the success of the well-known human genome project is primarily due to the establishment of rapid DNA sequencing techniques. The range of targets for analysis, detection and characterization has been extended from simple systems to complex ones. Complex systems consist of many different substances appearing in diversified morphologies, and some components are very tiny and they interact with each other nonlinearly. Advanced analysis methods, sensitive detection techniques, and perfect instrumentation are necessary to carry out qualitative and quantitative analysis in situ and transiently. They should be effective for analyzing huge data, detecting trace substances, and probing the biological activity.

Major challenges include:

(a) Separation and characterization of complex systems
(b) New analysis and detection tools in multiple dimensions, scales and parameters
(c) New methods and technologies in combinatorial chemistry
(d) Theory and methods for interaction and signal transformation of substances
(e) Analysis and detection methods and technologies for the national security and human health

6. Chemical Processes in Life System and Regulation of Function

Chemical biology, a term coined by a Harvard scientist Schreiber, represents an active field nowadays of understanding biology in light of chemistry. This area is an extension and a unification of biological organic, inorganic, structural, and natural product chemistry. It aims at exploring the biological effects and regulation of functions at molecular level. A central subject in the field is the selection from natural or synthetic small compounds such molecules that can regulate the genomic functions, signal transduction, and protein-cell interactions in biological systems and processes. These molecules work as probes and tools for studying the mechanisms of their interaction and recognition with targets in biological networks. Chemical biologists are also to discover the general rules of biological synthesis in nature. By doing so, they can devise effective, combinatorial strategies to synthesize more diversified molecules that may be good precursors for new drugs. Another important subject is to develop reliable techniques for analyzing complex biological systems either statically or dynamically. Fundamentally, chemical biology can help reveal the interaction of large molecules and information transfer in life systems at molecular level.

Major challenges include:

(a) Functional regulation of known biomolecules and their networks with small molecules
(b) Discovering small bioactive molecules and exploring their mechanisms of interaction with biological targets

Cheng et al.; Vision 2025: How To Succeed in the Global Chemistry Enterprise
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

(c) Improving methods and technologies for acquiring information in biological processes
(d) Discovering new biological targets and networks based on small-molecule probes
(e) Explaining the chemical nature of life processes

7. Fundamental Questions in Green and Environmental Chemistry

Environmental chemists mainly focus on the measurements and control of the existence, characterization, behavior, and effects of chemical substances in different environmental media. Environmental chemistry is typically an interdisciplinary field, which is different from traditional chemistry in the scale of time and space. Understanding the chemistry in environmental sciences is essential to solving the pollution problems. Because environmental pollution aggravates with rapid industrialization, Chinese chemists should contribute more to protect the natural surroundings and ecologic systems.

As indicated earlier, environmental chemistry plays important roles in monitoring, detecting, categorizing the sources of pollution, understanding the related chemical and ecological processes and effects, and controlling as well as preventing chemical pollutions. However, to entirely get rid of the environmental problems, one has to resort to green chemistry. The mission of green chemistry is to "promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substance in the design, manufacture, and use of chemical products" (see the website of U.S. Environmental Protection Agency). Aiming at sustainable development, green chemists perform the cutting-edge research for manufacturing safer products and reducing waste, energy, and resources. The final goal is to develop environmentally friendly means of chemical production. Green chemistry will eventually result in a revolutionary change in chemical sciences and should be a sound basis for a sustainable and harmonious development of modern society.

Major challenges in green chemistry include:

(a) Highly effective and selective reactions and processes with atomic economy
(b) Development and use of environmentally friendly reaction media
(c) Transformation of use of recycled materials, biodegradable materials and biomass
(d) Integration of processes based on green chemistry

Major challenges in environmental chemistry include:

(a) Automatic, online, in situ, dynamic, and transient analysis of pollution
(b) Understanding and predicting transport rule, ecological risk, and health effects of persistent poisonous and hazardous substances
(c) Fundamental principles and methods for controlling pollution
(d) Environmental molecular sciences

(e) Applications of biological, information, and material techniques in environmental chemistry

8. Chemistry of Material Science

Materials, information and energy are the indispensable tripod for modern civilization. Certainly, materials are essential for humankind to survive and to exploit. Molecular design, synthesis, elucidation of structure and properties of materials, and mechanisms of surface reactions are all core subjects in traditional chemical sciences. Chemistry is no doubt the cradle of new materials. The last two decades witnessed much progress in material science, exemplified by the discovery of numerous functionalized molecules. They include electro-optical and magnetic polymers, fullerenes and carbon nanotubes, self-assembled monolayers, ferrocene catalysts, combinatorial materials, nanocrystals, and various industrial plastics, rubbers and fibers. Computer simulation of the structures and properties of complex materials as well as computer-assisted design becomes a powerful tool in material science.

Major challenges in chemistry of materials include:

(a) Relationships between the chemical structure-assembly morphology and properties
(b) Numerical simulation, syntheses, and synergistic effects of smart composite materials
(c) Design, pollution-free syntheses and stability of environmental friendly and biocompatible materials
(d) Control of the chemical synthesis and morphology under mild or extreme conditions
(e) Chemistry of failure and remediation processes of materials

9. Fundamental Chemistry in Energy and Resources

Manifesting a nation's comprehensive strength as well as standard of living and cultural achievements, energy and resources are the material basis for economic and social development. Nowadays, energy resources are so critical for sustainable development that the energy systems established last century no longer meet the current needs for high efficiency, cleanliness, economy, and safety. In China, there are many opportunities in the research on chemistry of coal, gas, and the transformation between coal and gas. To develop cutting-edge techniques in this and other resources such as solar, biological, and hydrogen energy is of high priority.

Major challenges include:

(a) Chemistry of effective, clean refining of fossil fuels
(b) Control and conversion of greenhouse gases
(c) Renewable and clean energies

Cheng et al.; Vision 2025: How To Succeed in the Global Chemistry Enterprise
ACS Symposium Series; American Chemical Society: Washington, DC, 2014.

(d) Chemistry of highly effective, clean battery
(e) Physical chemistry and utilization of specific resources in China

10. Essential Scientific Questions in Chemical Engineering

Emerging from applied chemistry, chemical engineering is an academic discipline on mass transport, energy transfer, and other related processes in manufacturing chemical products. Its goal is to improve the quality of chemical industry with the expertise from chemistry, physics, and mathematics. Chemical engineers focus on the study of the dependence of reactions on mass transport in industry. They develop new approaches for amplification, and control of matter transformation, and the design of equipments for effective, energy saving, economy, and safe production.

Major challenges include:

(a) Fundamental theory of chemical engineering for large-scale manufacturing and applications of advanced materials
(b) Chemical reaction, biological transformation and ultra-large separation processes
(c) Numerical simulation and information acquisition, retrieval, and applications of chemical engineering processes
(d) Control of the complex structures in chemical engineering

Perspective

Chemistry has indeed contributed largely to the social development and civilization. It can be seen in every corner of human activities, from plastics and daily consumables, food and nutrition, drugs and genome project to energy and transport, materials and information technology. Although chemistry has tremendously profited the modern society, unfortunately its image has been tarnished by the negative publicity associated with pollution of chemical industry, green house effects, and other environmental problems. It is the scientists' mission to build a consensus with the society that these negative effects can be remedied only through the advancements in science. Thus, general chemical education is a necessary responsibility for all chemists worldwide. We should tell people that chemistry, through further advancements instead of retrogradations, can provide solutions to problems ranging from global warming, pollution, resources limitation to food shortage and fatal diseases and epidemics. In summary, chemistry is one of the key scientific foundations for the sustainable development of a harmonious society.

Acknowledgments

We take this opportunity to express our sincere gratitude towards many colleagues for constructive suggestion and insightful comments. We are indebted to Prof. Chunli Bai, the President of Chinese Academy of Sciences and the Past President of the Chinese Chemical Society, for sharing his broad vision on chemistry with us. He proof-read and made corrections on the first draft of this article. We are especially indebted to Prof. Jiannian Yao, President of the Chinese Chemical Society and Vice-President of the National Natural Science Foundation of China, for his constant support in international activities of CCS and for sharing his opinions on the advances of chemical sciences in China. The authors also thank Prof. Wenping Liang and Yongjun Chen, Directors of the Department of Chemical Sciences of the National Natural Science Foundation of China (NSFC), for providing the General Outline of Chemical Sciences Development in China. The following scientists have provided invaluable research highlight (alphabetic order): Chunli Bai, Yong Cao, Song Gao, Maochun Hong, Guibin Jiang, Shuhua Li, Yadong Li, Wanzhen Liang, Wenjian Liu, Shengming Ma, Yanlin Song, Shigang Sun, Zhongqun Tian, Chen-Ho Tung, Lijun Wan, Deyue Yan, Jinlong Yang, Xueming Yang, Jiannian Yao, Dongyuan Zhao, Jincai Zhao, Lansun Zheng and Qilin Zhou. We would like to apologize any inaccurate presentation of other's work. The authors are indebted to Dr. Huaping Xu for careful proofreading of the manuscript and making corrections and adjustments of the tables, schemes, figures, and references.

References

1. Bai, C. L. *Chin. Sci. Bull.* **2009**, *54*, 1941.
2. Zhou, H. H.; Song, Y. L. *Adv. Mater. Res.* **2011**, *174*, 447.
3. Yao, X.; Song, Y. L.; Jiang, L. *Adv. Mater.* **2011**, *23*, 683.
4. Tian, D. L.; Song, Y. L.; Jiang, L. *Chem. Soc. Rev.* **2013**, *42*, 5184.
5. Zhang, Z. L.; Zhang, X. Y.; Xin, Z. Q.; Deng, M. M.; Wen, Y. Q.; Song, Y. L. *Nanotech.* **2011**, *22*, 425601.
6. Zhao, A. D.; Li, Q. X.; Chen, L.; Xiang, H. J.; Wang, W. H.; Pan, S.; Wang, B.; Xiao, X. D.; Yang, J. L.; Hou, J. G.; Zhu, Q. S. *Science* **2005**, *309*, 1542.
7. Wang, X.; Zhuang, J.; Peng, Q.; Li, Y. D. *Nature* **2005**, *437*, 121.
8. Chen, T.; Yang, W. H.; Wang, D.; Wan, L. J. *Nat. Commun.* **2013**, *4*, 1389.
9. Xie, S. Y.; Gao, F.; Huang, R. B.; Wang, C. R.; Zhang, X.; Liu, M. L.; Deng, S. L.; Zheng, L. S. *Science* **2004**, *304*, 699.
10. Tian, N.; Zhou, Z. Y.; Sun, S. G.; Ding, Y.; Wang, Z. L. *Science* **2007**, *316*, 732.
11. Chen, H. J.; Guo, Y. L.; Yu, G.; Zhao, Y.; Zhang, J.; Gao, D.; Liu, H. T.; Liu, Y. Q. *Adv. Mater.* **2012**, *24*, 4618.
12. Zhang, J.; Geng, H.; Virk, T. S.; Zhao, Y.; Tan, J. H.; Di, C. A.; Xu, W.; Singh, K.; Hu, W. P.; Shuai, Z. G.; Liu, Y. Q.; Zhu, D. B. *Adv. Mater.* **2012**, *24*, 2603.

13. Zhang, F. J.; Di, C. A.; Berdunov, N.; Hu, Y. Y.; Hu, Y. B.; Gao, X. K.; Meng, Q.; Sirringhaus, H.; Zhu, D. B. *Adv. Mater.* **2013**, *25*, 1401.
14. Feng, F. D.; Liu, L. B.; Wang, S. *Nat. Protoc.* **2010**, *5*, 1255.
15. Xing, C. F.; Xu, Q. L.; Tang, H. W.; Liu, L. B.; Wang, S. *J. Am. Chem. Soc.* **2009**, *131*, 13117.
16. He, Y. J.; Chen, H. Y.; Hou, J. H.; Li, Y. F. *J. Am. Chem. Soc.* **2010**, *132*, 1377.
17. Huang, F.; Hou, L. T.; Wu, H. B.; Wang, X. H.; Shen, H. L.; Cao, W.; Yang, W.; Cao, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9845.
18. Zeng, W. J.; Wu, H. B.; Zhang, C.; Huang, F.; Peng, J. B.; Yang, W.; Cao, Y. *Adv. Mater.* **2007**, *19*, 810.
19. He, Z. C.; Zhong, C. M.; Su, S. J.; Xu, M.; Wu, H. B.; Cao, Y. *Nat. Photon.* **2012**, *6*, 591.
20. Zhang, C.; Yan, J.; Yao, J. N.; Zhao, Y. S. *Adv. Mater.* **2013**, *25*, 2854.
21. Lei, Y.; Liao, Q.; Fu, H. B.; Yao, J. N. *J. Am. Chem. Soc.* **2010**, *132*, 1742.
22. Wan, Y.; Zhao, D. Y. *Chem. Rev.* **2007**, *107*, 2821.
23. Yan, D. Y.; Zhou, Y. F.; Hou, J. *Science* **2004**, *303*, 65.
24. Gao, C.; Yan, D. Y. *Prog. Polym. Sci.* **2004**, *29*, 183.
25. Wang, C.; Wang, Z. Q.; Zhang, X. *Acc. Chem. Res.* **2012**, *45*, 608.
26. Wang, Y. P.; Ma, N.; Wang, Z. Q.; Zhang, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 2823.
27. Wang, C.; Ying, S. C.; Xu, H. P.; Wang, Z. Q.; Zhang, X. *Angew. Chem., Int. Ed.* **2008**, *47*, 9049.
28. Li, H. R.; Wu, L. Z.; Tung, C. H. *J. Am. Chem. Soc.* **2000**, *122*, 2446.
29. Tung, C. H.; Wu, L. Z.; Zhang, L. P.; Chen, B. *Acc. Chem. Res.* **2003**, *36*, 39.
30. Feng, K.; Zhang, R. Y.; Wu, L. Z.; Tu, B.; Peng, M. L.; Zhang, L. P.; Zhao, D. Y.; Tung, C. H. *J. Am. Chem. Soc.* **2006**, *128*, 14685.
31. Xie, J. H.; Zhou, Q. L. *Acc. Chem. Res.* **2008**, *41*, 581.
32. Zhu, S. F.; Zhou, Q. L. *Acc. Chem. Res.* **2012**, *45*, 1365.
33. Li, S.; Zhu, S. F.; Zhang, C. M.; Song, S.; Zhou, Q. L. *J. Am. Chem. Soc.* **2008**, *130*, 8584.
34. Xie, J. H.; Liu, X. Y.; Xie, J. B.; Wang, L. X.; Zhou, Q. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 7329.
35. Zhu, S. F.; Cai, Y.; Mao, H. X.; Xie, J. H.; Zhou, Q. L. *Nat. Chem.* **2010**, *2*, 546.
36. Zhu, B. Z.; Zhao, H. T.; Kalyanaraman, B.; Liu, J.; Shan, G. Q.; Du, Y. G.; Frei, B. *Proc. Natl. Acad. Sci. U.S.A* **.2007**, *104*, 3698.
37. Zhu, B. Z.; Kalyanaraman, B.; Jiang, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 17575.
38. Zhao, W.; Ma, W. H.; Chen, C. C.; Zhao, J. C.; Shuai, Z. G. *J. Am. Chem. Soc.* **2004**, *126*, 4782.
39. Qiu, M. H.; Ren, Z. F.; Che, L.; Dai, D. X.; Harich, S. A.; Wang, X. Y.; Yang, X. M.; Xu, C. X.; Xie, D. Q.; Gustafsson, M.; Skodje, R. T.; Sun, Z. G.; Zhang, D. H. *Science* **2006**, *311*, 1440.
40. Deng, W. H.; Xiao, C. L.; Wang, T.; Dai, D. X.; Yang, X. M.; Zhang, D. H. *Science* **2010**, *327*, 1510.

41. Li, J. F.; Huang, Y. F.; Ding, Y.; Yang, Z. L.; Li, S. B.; Zhou, X. S.; Fan, F. R.; Zhang, W.; Zhou, Z. Y.; Wu, D. Y.; Ren, B.; Wang, Z. L.; Tian, Z. Q. *Nature* **2010**, *464*, 392.
42. Liu, Z.; Ding, S. Y.; Chen, Z. B.; Wang, X.; Tian, J. H.; Anema, J. R.; Zhou, X. S.; Wu, D. Y.; Mao, B. W.; Xu, X.; Ren, B.; Tian, Z. Q. *Nat. Commun.* **2011**, *2*, 305.
43. Liu, T. F.; Fu, D.; Gao, S.; Zhang, Y. Z.; Sun, H. L.; Su, G.; Liu, Y. J. *J. Am. Chem. Soc.* **2003**, *125*, 13976.
44. Wang, X. Y.; Wang, L.; Wang, Z. M.; Gao, S. *J. Am. Chem. Soc.* **2006**, *128*, 674.
45. Liu, W. J. *Mol. Phys.* **2010**, *108*, 1679.
46. Li, S. H.; Li, W.; Fang, T. *J. Am. Chem. Soc.* **2005**, *127*, 7215.
47. Li, S. H.; Shen, J.; Li, W.; Jiang, Y. S. *J. Chem. Phys.* **2006**, *125*, 074109.
48. Liu, J.; Liang, W. Z. *J. Chem. Phys.* **2011**, *135*, 184111.
49. Liu, J.; Liang, W. Z. *J. Chem. Phys.* **2011**, *135*, 014113.
50. Peng, Q.; Yi, Y. P.; Shuai, Z. G.; Shao, J. S. *J. Chem. Phys.* **2007**, *126*, 114302.
51. Peng, Q.; Yi, Y. P.; Shuai, Z. G.; Shao, J. S. *J. Am. Chem. Soc.* **2007**, *129*, 9333.
52. Shuai, Z. G.; Wang, L. J.; Li, Q. K. *Adv. Mater.* **2011**, *23*, 1145.
53. Geng, H.; Peng, Q.; Wang, L. J.; Li, H. J.; Liao, Y.; Ma, Z. Y.; Shuai, Z. G. *Adv. Mater.* **2012**, *24*, 3568.