

The research front on molecular functional switches

— A special issue on organic photoswitchable multifunctional molecules and materials

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The 4th International Workshop on Organic Photoswitchable Multifunctional Molecules and Materials was held between 25th and 27th October 2009 in East China University of Science & Technology (ECUST), Shanghai. It was a great event for academic circles, and at the same time provided an excellent chance for communication between international scholars from the field of organic photoswitchable functional materials. Along with a successful series of workshops on this topic, such as those held by Japan-France (Shonan, 2006), France-Russia (Saissac, 2007) and France-Japan (Arras, 2008), ECUST (China) and CNRS's GDRI (France) joined together to host this continued workshop on novel photoswitchable multifunctional molecules and materials. This workshop covered all aspects from molecular design to devices using photo-switchable materials, and was intended as a forum for further interdisciplinary discussion and international cooperation. The workshop was presided over by Prof. Yu Pei and Prof. He Tian. During the workshop, more than 50 experts and 50 Ph.D. candidates from Canada, Germany, Italy, Hong Kong, France, Japan, South Korea, Sweden, Singapore, the USA and China presented and discussed the latest research findings, interpretations and ideas relating to organic photoswitchable multifunctional materials. Many famous professors came to the gathering, with the aim of better promoting the development of advanced materials and also mutual understanding.

Following the workshop, we have received 17 high quality papers from the scholars for a special issue of *Frontiers of Chemistry in China*. This issue provides a unique opportunity for scientists in this area to exchange ideas and share in the achievements in the field of organic functional materials, mainly focussing on organic chemosensors and photochromic molecules. As we know, the most convenient way to introduce a photoswitching function into a molecular system is to use photochromic units as photo-functional units. A particularly interesting photochromic unit is diarylethene, which reversibly changes its π -conjugation and structure upon irradiation. In this

workshop, many lectures were given on photochromic diarylethenes. Therefore, taking into consideration the requirements of most international participants, we decided to launch another special issue on the topic of photochromic molecules, namely *Dyes and Pigments* (Guest Editors: Prof. Neil Branda and Prof. He Tian), which will include papers mostly from foreign scientists. Of course, this issue in *Frontiers of Chemistry in China* should reflect some of the progress in the photochromic field in China. Two research articles by Prof. Yi Chen et al. and Prof. Shou-Zhi Pu et al. report new photochromic diarylethene compounds for holographic optical recording and two-photon absorption, respectively.

Owing to their direct toxic effects on human beings, animals and plants, chemical warfare agents (CWAs) and their mimics have become widespread in agriculture and chemical warfare. A short review by Prof. Chun-Hua Yan and his coworkers contains recent reports on the design of fluorescent molecular switches and their advantages in the detection of CWAs. It is believed that extensive interest in this field has accelerated the development of novel fluorescent molecular switches and detection techniques. Seven research articles (from the groups of Yun-Bao Jiang, Xiao-Jun Peng, Jian-Zhang Zhao, Wei-Hong Zhu, Jian-Li Hua, Juan Xie and Yong-Shu Xie) show how to construct new organic fluorescent sensing molecules with highly selectivity and sensitivity and even with a new signal-transduction mechanism. It is interesting to note that a new switching molecule based on ferrocene can be controlled and detected by an aggregation-induced emission (AIE) phenomenon (research article by Dr. Dong Zhang).

For organic compounds, switching at the molecular level is important in materials for sensing, separation, and drug delivery. In response to changes in temperature, concentration, media, light, time, and the presence or absence of other ions or molecules, organic compounds can aggregate or de-aggregate, which triggers various chemical, physical, and biological phenomena. Prof. Shu Wang and his coworkers prepared a water-soluble conjugated polyfluorene with



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pendant carboxylate and amine moieties for use as a pH-responsive contrast agent (PFP-aa/Gd) in magnetic resonance imaging (MRI) by binding to Gd (III). As the pH changes from 10 to 4, both the carboxylate and amine moieties are protonated. Thus PFP-aa exhibits a positive charge and forms tight aggregations, which reduce molecular tumbling and accelerates the exchange of bound water, making PFP-aa/Gd suitable as a potential marker of pH values below physiological level. In addition, organogels (or molecular gels) present original morphologies fascinating properties. Prof. Tao Yi et al. reported a novel type of ligand 1,4,7,10-tetraazacyclododecane, functionalized with azobenzene moieties grafted with two alkyl chains, which can form metallogels in the presence of a Zn(II) cation. The driving forces of the gel formation are attributed to intermolecular hydrophobic interactions between the alkyl chains and π - π interactions between the azobenzenes. This system has dual functions, both for metal ion sensing and as a low molecular weight metallogel.

By changing the position of structurally incorporated chromophores, synthesis of dendrimers with different sensing properties can be achieved. Prof. Jian Pei has reviewed another approach using chromophore-containing dendrimers for sensing applications. Judicious tailoring of the dendrimer architecture has resulted in enhanced selectivity and sensitivity. They pointed out there is still room for extensive development in this area. The application of chromophore-functionalized dendrimers in sensors is still in its early stages, and much work should be done to fully explore the potential of such a combination of structural elegance (dendrimer structure) and practical application (sensors). The disassembled dendrimers represent a good example in this direction. We might also think of other phenomena, characterized by use of conjugated units, could be utilized to this end. Colloidal semiconductor nanocrystals (NCs), often referred as quantum dots (QDs), are also of great interest for both fundamental study and technical applications such as fluorescent labeling. In this issue, one paper by Prof. Xin-Hua Zhong and his coworkers about the preparation of high-quality CdSe/CdS/ZnS double shelled core/shell nanostructures via a facile and economical route is included. This work may find future application in making nanocrystals in large quantities.


A novel strategy for optical sensors using tunable photonic crystals (PCs) as a new type of label-free spectrum-encoding carrier has been described by Prof. Yan-Lin Song. These PCs hold great promise for the design of affinity matrices capable of detecting environmental changes through simple monitoring of the bandgap peak position, using standard spectrophotometric techniques or directly by the naked eye. They can be used as self-reporting sensors to measure various environmental changes such as pH, the presence of analytes

or metal ions, humidity and other physical deformations. Moreover, they can remarkably enhance detection based on fluorescence techniques, due to their capability to confine and control the propagation of light with minimal loss. Of course, there are still a lot of challenges in practical application, for example how to reduce crystal defects. We believe that PCs will throw new light on the study of novel optical sensors, as shown in the cover picture of this special issue.

Although photovoltaics have been dominated by devices based on crystalline or amorphous silicon-based solar cells, recent attention has been paid to mesoscopic inorganic and organic bulk-junction devices with low fabrication costs and flexible substrates. The most advanced of these new devices is the dye-sensitized solar cell (DSSC). Organic dyes with a D- π -A structure have encouraged increasing attention as sensitizers in DSSCs, due to their rich photophysical properties, easy molecular tailoring, and low-cost dye production. This special issue includes a review by Prof. Zhong-Sheng Wang mainly focusing on the relationship between dye structure and photovoltaic properties.

Editing this special issue for *Frontiers of Chemistry in China* has been both an honour and a pleasure. Obviously, the progress in organic photoswitchable functional materials in China cannot be comprehensively covered in a single journal issue, and we apologize sincerely to those who might feel their work has been omitted. We would like to take this opportunity to express our greatest thanks to Prof. Yu-Liang Yang, the Editor-in-Chief of this journal and all referees. Special thanks go to Dr. Lin Tian (Chief of the Editorial Office) and the journal office of *Frontiers of Chemistry in China* for their valuable support and guidance in the preparation of this special issue. Nevertheless, I hope that this cluster of papers is able to capture the excitement and challenges that pervade the study of molecular switches.

Enjoy!



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Guest Editor

Prof. He TIAN received his Ph.D. degree in 1989 from East China University of Science & Technology (ECUST) (Shanghai, China). In 1999, he was appointed Cheung Kong Distinguished Professor by the Education Ministry of China. His current research interests include the syntheses of novel functional organic dyes and polymers, as well as development of interdisciplinary materials science that determines the electronic and optical properties of materials. Prof. Tian has published over 260 papers in international journals and has been awarded 55 Chinese patents. Prof. Tian is an Associate Editor of *Dyes and Pigments* (Elsevier) and an Advisory Board Member for *Polymer Chemistry* (RSC).