

MATERIALS SCIENCE

Diverge from the norm

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It has been a general belief that luminophore aggregation normally quenches light emission. The conceptualization of ‘aggregation-induced emission’ (AIE) breaks this ‘common law’ and provides a new stage for the exploration of practically useful light-emitting materials. The booming development in this emerging area of research has recently been showcased at the First International Symposium on Aggregation-Induced Emission (ISAIE) held in Wuhan, China.

A burning desire of research scientists is to discover exotic phenomena or wonder processes that ‘violate the norm’ or ‘break the rule’ because the decipherment of such phenomena or processes may forge new concepts that may change people’s way of thinking. A general belief in the area of research on luminescence is ‘concentration quenching’—an effect ‘common to most aromatic hydrocarbons and their derivatives’, as taught by Birks in his classical photophysics book [1]. Since the concentration quenching effect is often associated with chromophore aggregation processes, it is thus also known as aggregation-caused quenching (ACQ). In 2001, a Chinese research team led by B Z Tang of The Hong Kong University of Science & Technology (HKUST) found that a group of organosilicon complexes such as hexaphenylsilole (HPS) were non-fluorescent as single molecules but became emissive when assembled or aggregated [2,3]. Tang coined the term of AIE to describe this abnormal luminescence phenomenon [2]. Since the new AIE effect is diametrically opposite to the conventional ACQ effect, it is of great academic value and has far-reaching practical implications. The potential of generating new knowledge through investigating the unusual process has attracted many researchers to the AIE study. Thanks to their enthusiastic

efforts, great progresses have been made in the area of AIE study in the past decade. An international symposium dedicated to the AIE research has recently been held in Wuhan to bring active AIE researchers together to review past accomplishment and to discuss future development.

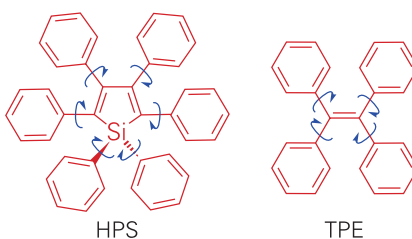


Figure 1. The two star molecules of AIE family.

ISAIE was hosted by Wuhan University on 17–20 May 2013. It was supported by the Ministry of Science & Technology and the National Natural Science Foundation of China, chaired by Li of Wuhan University and Tang of HKUST, and attended by about 160 people from China, US, Japan, Korea and Singapore. The attendees vehemently shared their new research findings and vigorously discussed important issues in the field during the three-day meeting. The presentations and discussions covered many topics, including the understanding of

working mechanisms of AIE processes, development of new AIE luminogen systems, and exploration of their unique high-tech applications.

How an AIE process works is an issue of great importance, for a clear understanding of its operating principle is of guiding value to the research endeavors of designing new AIE systems and expanding the territory of AIE study. A number of hypotheses have been proposed and put to the test in the past decade. Over the years, the restriction of intramolecular rotation (RIR) of aromatic rotors in the aggregates of AIE luminogens has gained general acceptance as the main cause of the AIE processes. The RIR mechanism was well supported by the new experimental results and theoretical simulations presented by the attendees at the ISAIE meeting. J-L Hong from Taiwan, for example, talked about his group’s work on taking ‘rigid, bulky fragment with high rotational energy barrier’ and ‘specific forces such as hydrogen and ionic bonds’ as internal and external strategies, respectively, to study the ‘factors controlling molecular rotation of

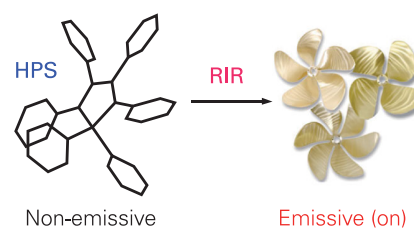


Figure 2. Restriction of intramolecular rotation (RIR). Phenyl rotors in a single HPS molecule readily undergo dynamic intramolecular rotation, which non-radiatively annihilates the excited states, making HPS non-luminescent in a dilute solution. In the aggregates of HPS molecules, the intramolecular rotation is restricted due to the involved physical constraint. This RIR process blocks the non-radiative relaxation pathway and opens the radiative decay channel, thus rendering the HPS aggregates highly emissive.

non-coplanar luminogens'. Z Shuai from Beijing, a well-known theoretician, employed the quantum and molecular mechanics to show that intramolecular motion plays an essential role in the photophysical processes of a series of AIE luminogens.

The RIR mechanism suggests that propeller-shaped molecular rotors are promising candidates for AIE luminogens. This proves to be true: a large variety of molecular rotors have been found to be AIE luminogens by many research groups in the past decade [4–9]. A typical example of a rotor-like molecule is tetraphenylethylene (TPE), which has become one of the most extensively studied AIE luminogens, due to its simple synthesis and facile structural derivatization. A number of new AIE systems were reported at the ISAIE meeting. T Shimizu of Kyoto Institute of Technology, for example, presented a series of diaminobenzene-cored AIE luminogens, A Tong of Tsinghua University disclosed a group of AIE-active Schiff bases with easy synthetic accessibility, H Dong and W Hu from Chinese Academy of Sciences unveiled a novel tetracyanoanthraquinodimethane-based AIE system, K Tanaka and Y Chujo of Kyoto University discussed their organoboron polymers with AIE attribute, and Qin of Zhejiang University talked about a family of AIE polymers synthesized from 'click' polymerization. While Li of Wuhan University created deep-blue AIE luminogens, H Tian of East China University of Science & Technology (ECUST) and D Zhang of Chinese Academy of Sciences developed AIE systems with far-red/near-IR emission. Remarkably, W Yuan of Shanghai Jiao Tong University uncovered that the crystals of simple aromatic acids and esters emitted efficient phosphorescence at room temperature. The zealous efforts of the AIE researchers have resulted in a bumper harvest—the generation of a variety of new AIE systems with luminescence quantum yields up to unity and emission colors covering the whole visible spectral range with extension well to the near-IR region.

A large portion of the oral talks and poster presentations at the ISAIE

meeting was devoted to the exploration of new photophysical processes of the AIE luminogens and the demonstration of their unique high-tech applications. The AIE luminogens have been found to exhibit reversible polymorphisms and distinct chromisms, largely due to their unique propeller-shaped molecular structures. Under appropriate conditions, the luminogens undergo morphological transformations between amorphous and crystalline states and among different crystalline phases. In response to various external stimuli (e.g. light, heat, stress, vapor, pH and time), the luminogens show multiple chromic effects (e.g. photo-, thermo-, piezo-, vapo-, acido- and chronochromisms). Taking advantage of the AIE process and making use of the RIR mechanism, the researchers have found an impressive array of technological applications for the AIE luminogens, particularly in the areas of optoelectronics, chemosensors and bioprobes.

Light emission of the conventional luminophores 'is often quenched in the solid state because of the typical ACQ effect, a thorny obstacle to high-performance organic optoelectronic materials', said W Zhu of ECUST. At the ISAIE meeting, he discussed crystal engineering in a quinolinemalononitrile-based red AIE system and demonstrated its application as low-loss optical waveguides, while J Hua from the same university presented the work of her team on the development of AIE luminogens with large optical nonlinearity or multiphoton susceptibility. The laboratory of F C Pigge at the University of Iowa has been 'engaged in the studies that seek to capitalize upon not only fluorescent properties of TPE derivatives but also their potential redox activities and structural features to ultimately design new optoelectronic organic materials and fluorescent crystalline assemblies.' D Jiang's group at Okazaki Institute for Molecular Science has developed a strategy for the construction of TPE-based microporous networks with extended electronic conjugation, facilitated exciton migration and enhanced emission efficiency. These assemblies and networks have been found to work as excellent chemosensors

with high sensitivity. The AIE-active mesoporous materials made by J Yu of Jilin University functioned as efficient and recyclable fluorescent sensors for the detection of explosive vapors and acidic or corrosive gases.

Since light-emitting species are often hydrophobic aromatic rings that are incompatible with aqueous media, traditional luminophores suffer from the severe ACQ problem when used for bioassay applications. Inorganic quantum dots (QDs), on the other hand, are cytotoxic. Nanoparticles of AIE luminogens (or AIE dots) are envisioned to be an organic version of QDs with biocompatibility. This possibility has been actively explored by many research laboratories in recent years. B Liu of National University of Singapore, for example, fabricated the AIE dots and demonstrated their applications in cell imaging, intracellular sensing, multimodal probing, long-term tracing and so on [10]. T Sanji of Tokyo Institute of Technology developed a new fluorescence turn-on system for the identification of biogenic amines by the carboxylic acid-modified TPE luminogens and demonstrated its utility in the quality control of food freshness through quantifying the concentration of histamine in a tuna fish matrix. The group of B-H Han in the National Center for Nanoscience and Technology functionalized TPE with carbohydrates and used the AIE luminogens to assay enzymes, lectins and toxins. The K^+ ion plays an important role in many physiological processes and S Liu's team at University of Science & Technology of China constructed K^+ bioprobes through the integration of AIE concept with supramolecular host-guest recognition between the K^+ ion and crown-ether ring. J Qian of Zhejiang University used nanomicelles to encapsulate red/near-IR AIE luminogens and successfully applied them for blood-vessel and brain-nerve bioimaging of live mice under multiphoton excitation.

Notwithstanding the impressive advancement, much needs to be done to further develop the area of AIE research, as pointed out by Tang in his speech in the closing ceremony of the ISAIE meeting. For example, how does intramolecular vibration affect luminescence

behavior? Or in other words, can the restriction of intramolecular vibration (RIV) in the chromophore aggregates be utilized to develop new AIE systems? Some experimental results suggest this possibility [11], but further studies are required to confirm RIV as an effective approach to new AIE luminogens. A number of unorthodox luminogen systems carrying no conventional chromophores (e.g. aromatic rings and double bonds) have been found to show AIE effects [3]. The electron-rich elements, such as oxygen and nitrogen, in these non-traditional luminogens may have formed electronically conjugated atomic clusters in the aggregates, the real causes of which, however, remain to be carefully tackled and understood. While many fluorescent AIE systems have been developed, phosphorescent systems based on pure organic luminogens have been much less studied. Great research efforts should be devoted to the development of such systems because of their fundamental importance and practical implications. As AIE is a 'solid' effect (noting that an aggregate is a solid), much more applications can be expected and should be explored, taking into consideration

that luminescent *molecules* are used as real *materials* commonly in the solid state.

The ISAIE meeting was heralded as a great success by many attendees. Many of them are actually the witnesses of the rapid development in the emerging area of AIE study. There was only one AIE paper published in 2001, whereas the number of AIE publications has grown exponentially in recent years. A similar trend is observed in the citation pattern, with more than 4500 cites registered in 2012 alone. The numbers of papers and citations are anticipated to further grow in the years to come. The surging interest in the AIE research is anticipated to lead to the generation of more AIE luminogens with even higher quantum yields of luminescence and a wider range of emission colors, the establishment of clearer models and theorems for deeper understanding of the operating principles and working mechanisms of the AIE processes, and the invention of high-tech devices and systems based on the AIE luminogens for real-world practical applications in engineering robust forms. The second ISAIE meeting will be held in Guangzhou City, hosted by South China University of Technology, and chaired by Qin and

Tang in 2015. It is hoped that the biyearly ISAIE meeting will serve as a stage for AIE researchers to exchange information and ideas for pushing the AIE research to a wider scope with a newer height.

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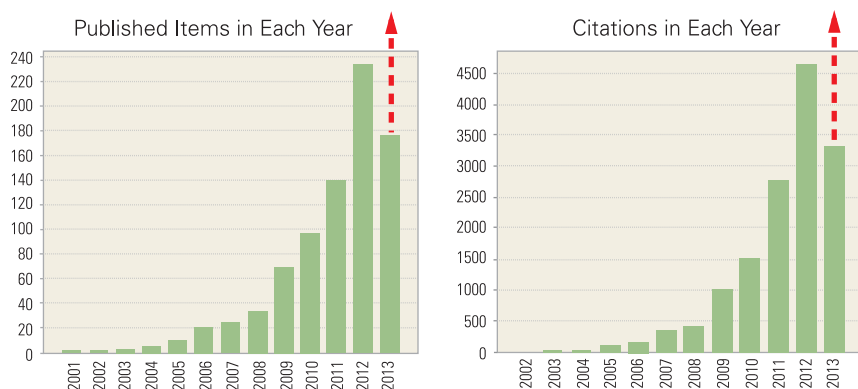


Figure 3. Surging interest. The numbers of papers and citations on AIE have been increasing exponentially in recent years. Data retrieved from *Web of Science* using the keyword of 'Aggregation-Induced Emission' on 22 August 2013.