## 光子鼻与分子材料团队简报

Newsletter of Photonic Nose and Molecular Materials Group
6 / 2022



六月大事记 Events in June, 2022	P2 - 3
毕业生动态 Alumni News	P4 - 7
科研亮点 Research Highlights	P8 - 18
交流合作 Exchange and Cooperation	P19 - 20
心绪感悟 Thoughts and Reflections	P21 - 22

#### 六月大事记 Events in June, 2022



#### 房喻院士亮相"院士说专业"特别节目 Fang Yu speaks on special program to would-be college students

6月24日,房喻院士亮相2022 高招季《院士说专业》特别节目, 为同学们讲述师范教育的光荣与职 责和化学学科的魅力和力量。

房喻院士讲到: "一个人遇到好老师是人生的幸运,一个学校拥有好老师是学校的光荣,一个民族源源不断涌现出一批又一批好老师则是民族的希望。"老师是一个光荣神圣而又责任重大的职业,一个好老师要"有理想信念、有道德情操、有扎实学识、有仁爱之心"。他还希望同学们学习作为创造性力量和有关物质的艺术的化学,成为创新性人才。

该节目由中国青年报社、中

国工程教育专业认证协会、教育部教育质量评估中心,联合9家全国性行业协(学)会、10所高校共同打造,于6月21日上线,11位院士详细解答考生关心的专业问题。

On June 24, Prof. Fang Yu spoke about the charms and powers of the chemistry discipline, to would-be college students who had finished their college entrance exams, on the special program "Academicians Talking About Majors" in 2022 higher institution admission season.

"It is fortunate for a person to encounter a good teacher, it is a pride of a school to have good



"一个人遇到好老师是人生的幸运,一个学校拥有好老师是学校的光荣,一个民族源源不断 重大的职业。一个好老师要"有理想信念、有道德情操、有扎实学识、有仁爱之心"。现代社结 求,需要师范教育更注重师范生持续发展能力和素质的培养。中国青年报、教育部教育质量评估 院院士、陕西师范大学原校长房喻为同学们详尽解答有关"师范生"的报考疑问。(中青报中环

#### 六月大事记 Events in June, 2022

teachers, and it is the hope of a nation for it to have generations of good teachers." Fang said on the program. A sacred profession with honor and duty, teaching requires a teacher to have ideals and beliefs, to be morally sound, to be knowledgeable and have a loving

heart. He also hoped the students would learn chemistry, which is a creative power and an art of matter, and become creative talents.

The program, in which eleven CAS academicians speak about issues of interest to college entrance examinees, is sponsored by the China

Youth newspaper, China Association for Professional Certification of Engineering Education, and Education Quality Assessment Center of Ministry of Education with the support of nine national associations and ten universities, and was aired on June 21.

# 房喻院士将受邀出任 ICM 杂志顾问编委 Fang Yu invited to serve on editorial advisory board of Industrial Chemistry and Materials

受中国科学院过程工程研究 所张锁江所长邀请,房喻院士 将出任过程所与英国皇家化学 会创办的 Industrial Chemistry and Materials (ICM) 杂志的顾问编委。

此前,受主编赵进才院士邀请,房喻院士已经出任《化学进

展》编委。

Invited by Zhang Suojiang, director of the Institute of Process Engineering, Chinese Academy of Sciences, Prof. Fang Yu will serve on the advisory editorial board of the journal Industrial Chemistry and Materials (ICM), which is to be founded jointly by the Royal Society of Chemistry and IPE.

Previously, Prof. Fang has been serving on the editorial board of Progress in Chemistry, at the invitation of its editor-in-chief CAS academician Zhao Jincai.

## 房喻 FANG YU 中国国等原理之 及西特别大学等政长

#### 房喻院士赴砺剑防卫进行技术指导交流 Fang Yu offers technical guidance at SRED

6月18日,房喻院士赴深圳 砺剑防卫技术有限公司,了解公 司近期的经营情况和业务进展, 并与研发团队进行了技术交流。

交流会上,房喻院士听取了公司技术研发的工作进展以及未来技术发展方向的规划,对技术 疑难问题进行了解答,并认可砺 剑防卫从现有传感技术在爆炸物/毒品检测领域的应用进一步向气体检测、食品安全等领域拓展的技术发展规划。

On June 18, CAS academician Prof. Fang Yu visited Shenzhen Lijian Defense Technology Co., Ltd., inquiring about its business progress and conducting technological exchange with its R&D team.

At the meeting, Prof. Fang was briefed about the company's work progress in technological R&D and its future plan for technological development. He answered questions on technological difficulties, and affirmed Lijian's technological development plan of transitioning from application of sensing technologies in explosives and narcotics detection to areas of gas detection and food safety.

3

#### 团队毕业生祁彦宇博士获 河北省自然科学基金优秀青年基金资助 Alumnus Qi Yanyu supported by Hebei Natural Science Youth Fund



近日,河北省科学技术厅网站发布关于 2022 年度省级科技计划自然科学基金(第一批)拟立项项目名单,团队毕业生祁彦宇博士获得河北省自然科学基金优秀青年基金资助。

祁彦宇师从房喻院士,于 2019年6月从陕西师范大学毕业, 获理学博士学位。同年7月加入 深圳大学国家杰青杨楚罗教授课 题组从事博士后研究;2021年9 月加入河北师范大学化学与材料 科学学院。

祁彦宇目前以第一作者身份

在 Adv. Funct. Mater.、Chem. Sci.、ACS Appl. Mater. Interfaces 等专业期刊发表 SCI 论文 8 篇,主持国家自然科学基金委青年科学基金项目 1 项,中国博士后科学基金1 项,河北师范大学科技类基金项目 1 项。

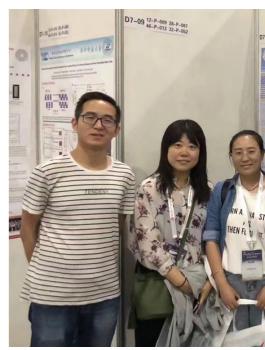
According to the 2022 list of first-batch projects supported by Hebei Province Science Program's Natural Science Fund by Hebei Provincial Department of Science and Technology released by Hebei Provincial Department of Science and Technology recently, Dr. Qi Yanyu, an alumnus of Fang Group is to be supported by the Youth Fund of Hebei Province Natural Science Fund.

Qi Yanyu graduated from Shaanxi Normal University in June, 2019 with a doctoral degree in Chemistry and his doctoral advisor is Prof. Fang Yu. He began to work as a postdoctoral fellow in National Science Fund Distinguished Young Scholar Prof. Yang Chuluo's research group at Shenzhen University in July, 2019, and joined Hebei Normal University's School of Chemistry and Materials Science in September, 2021.

He has published eight papers as the first author in SCI journals Adv. Funct. Mater., Chem. Sci., and ACS Appl. Mater. Interfaces, and hosted one National Natural Science Foundation's Youth Science Fund project, one China Postdoctoral Science Foundation project, and one Hebei Normal University Science Fund project.

祁彦宇(右二)、刘建飞(右一) 与房喻院士合影

Qi Yanyu (second from right) and Liu Jianfei (first from right) pose for a photo with Prof. Fang Yu



## 团队毕业生刘建飞博士入选 陕西省科协青年人才托举计划项目

Alumnus Liu Jianfei supported by Shaanxi AST Youth Talent Program

近日,陕西省科学技术协会 发布 2022 年陕西省科协青年人才 托举计划项目评审委员会评审结 果,团队博士毕业生刘建飞入选 企事业青年人才托举计划项目。

刘建飞,2018级博士研究生,师从房喻院士,获理学博士学位,现就职于西北有色金属研究院。迄今在Materials Chemistry Frontiers、ChemSusChem、Macromolecules等专业杂志发表论文多篇,获得2019年第五届"互联网+"大学生创新创业大

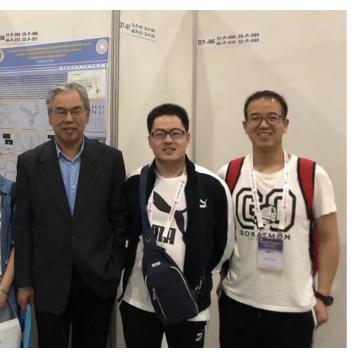


赛陕西赛区省级复赛(高教主赛 道)"银奖"。

> According to the results of 2022 Shaanxi Provincial Association of Science and Technology's Youth Talent Support Program announced by SPAST recently, Dr. Liu Jianfei. a class '21 alumnus of Fang Group, has been supported by the Enterprise and

Institution category of Youth Talent Support Program.

Liu Jianfei graduated from Shaanxi Normal University in 2021 with a doctoral degree in Chemistry before joining Northwest Nonferrous Metal Research Institute, and his doctoral advisor is Prof. Fang Yu. He has published several papers in journals of Materials Chemistry Frontiers, ChemSusChem, and Macromolecules, and won the silver award in the Shaanxi procince final of the Fifth "Internet +" College Student Innovation and **Entrepreneurship Competition** (Higher Education Main Track) in 2019.



#### 毕业生常兴茂博士应邀参加洪堡基金会年会 Alumnus Chang Xingmao attends Humboldt Foundation annual meeting



常兴茂在柏林自由大学洪堡年会 Chang Xingmao at Alexander von Humboldt Foundation annual meeting

6月22至23日,德国洪堡基金会(Alexander von Humboldt Foundation)年会在柏林举行,团队2019届博士毕业生常兴茂受邀参加。

常兴茂受洪堡基金会资助, 现作为洪堡学者(Humboldt research fellow)在德国乌尔姆大 学进行博士后研究。

6月22日,近600名洪堡学者参加了此次年会开幕式。柏林自由大学校长Gunter M. Ziegler教授和洪堡基金会主席Hans-Christian Pape教授出席开幕式并致辞。2020年诺贝尔化学奖获得者Emmanuelle Charpentier教授

分享了她关于基因工程的研究并 勉励年轻的科学家。23 日,与会 的洪堡学者们参观了德国总统官 邸贝尔维尤宫,并受到德国联邦 总 统 Frank-Walter Steinmeier 博 士的接见。常兴茂博士还参加了 关于 Machine Learning 的讲座。

洪堡基金会是为了纪念伟大的自然科学家和科学考察旅行家亚历山大·冯·洪堡于 1860 年建立的。洪堡基金会择优支持国外青年研究人员赴德国从事合作研究,洪堡基金以支持"个人成长"而非研究项目为导向,践行使洪堡学者在其学术生涯中终生受益的理念。

常兴茂表示,在会上有幸结 识了一大批不同领域的科研人员, 几乎涵盖了所有的理工科,也有 极个别的经济学、语言学博后。 通过和他们交流,真的长了不少 见识,以前不曾有这样的机会, 可以去体会不同学科学者对科研 的理解以及他们的思维方式。这 些人中搞化学的,国内出来的一 听我是陕师大来的,第一反应就 是房喻院士,我自然是发自内心 的偷偷开心, 也为是老师的学生 而自豪。现在想想老师总是不厌 其烦地给我们说着要走出去,要 多和不同领域的人打交道,真正 的走到这一步,才体会到老师的 良苦用心。在不费劲的情况下和 这些人建立起联系, 对未来在研 究道路上的发展是很有帮助的。

Dr. Chang Xingmao, a class '19 doctoral graduate of the group, was invited to attend the Alexander von Humboldt Foundation annual meeting held in Berlin, Germany on June 22 and 23.

Chang is now doing postdoctoral research as a Humboldt research fellow at the University of Ulm.

On June 22, Free University of Berlin president Gunter M.

Ziegler and Humboldt Foundation president Hans-Christian Pape spoke at the opening ceremony attended about 600 researchers from throughout the world. Prof. Emmanuelle Charpentier, the 2020 Nobel Prize Laureate in Chemistry, shared her research in genetic engineering and encouraged young scientists. On June 23, the Humboldt research fellows visited Schloss Bellevue, where they were received by Federal President Frank-Walter Steinmeier. Chang also attended the lecture about Machine Learning.

The Alexander von Humboldt Foundation for Nature Research and Travel was originally established in Berlin in honor of Alexander von Humboldt in 1860. Today, the Alexander von Humboldt Foundation promotes academic cooperation, international understanding, scientific progress and development between excellent scientists and scholars from abroad and from Germany. The Foundation promotes international understanding, scientific progress and development, aiming at the lifelong personal growth of the Humboldtians rather than focusing on research results.

Chang said that he was able to meet many researchers from different disciplines at the meeting, including almost all fields of science and technology, and some postdocs in economics and linguistics.

He gained a lot of insights from

talking to them, getting to know their understandings of research and ways of thinking, which was an opportunity he had for the first time. When some of the Chemists who are also from China heard I was from Shaanxi Normal University, their first response was academician Fang Yu. He felt so delighted and proud being

a student of Prof. Fang. He now felt the intention and earnestness of Prof. Fang, recalling him urging them repeatedly to go overseas to communicate with people from different backgrounds --- networking with these people in social occasions is beneficial in the future career development.



常兴茂在海德堡大学与 Frank Würthner 教授合影 Chang Xingmao with Prof. Frank Würthner at Heidelberg University



常兴茂在贝尔维尤宫 Chang Xingmao at Schloss Bellevue

7





A Journal of the German Chemical Society

Research Article

Through-Space Charge Transfer: A New Way to Develop High-Performance Fluorescence Sensing Film towards Opto-Electronically Inert Alkanes

Zhaolong Wang, Xinyu Gou, Qiyuan Shi, Ke Liu, Xingmao Chang, Gang Wang, Wenjun Xu, Simin Lin, Taihong Liu, Yu Fang 

▼

#### 跨空间电荷转移:光电惰性饱和烷烃荧光敏感 薄膜创新制备新策略

烷烃类化合物是重要的化工原料,易于挥发,易于燃烧,是工业生产安全的重要隐患。此外,小分子饱和烷烃是人体生理代谢的重要产物,作为消化道恶性病变的重要标示物,在挥发组学研究中已经广受关注。可以说,饱和烷烃气体的原位、在线、高灵敏、高选择、快速探测具有重要的意义。然而,饱和烷烃反应活性低,光电惰性,高性能探测极具挑战。

薄膜荧光传感是继离子迁移 谱之后,业界公认的有望替代嗅 爆犬、缉毒犬和疾病诊断犬的新 一代微痕量物质气相检测技术。 薄膜荧光传感器能耗低、结构相 对简单、易于实现便携。敏感薄 膜材料创制和高性能化是获得高 性能荧光传感器的关键,其核心 又是高性能荧光传感单元的设计 合成。 本工作中,我们采用跨空间 电荷转移分子设计策略,合成了 U形碳硼烷桥联花二酰亚胺 - 蒽 二分体,以其作为传感单元,实 现了对饱和烷烃类物质的气相高 性能检测。电子给体蒽与受体花 二酰亚胺间面对面的排列方式保证了分子内跨空间电荷转移过程的有效发生,导致该二分体呈现出显著的荧光双发射和溶致变色行为。借助超快瞬态吸收光谱技术,我们观察到了二分体受光激

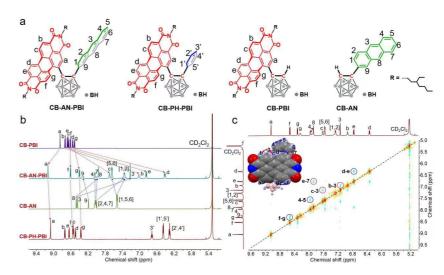


图 1. (a) 目标化合物 CB-AN-PBI 和对照化合物的化学结构式; (b) 目标化合物 CB-AN-PBI 和对照化合物的核磁对比; (c) 目标化合物 CB-AN-PBI 的  $^1$ H- $^1$ H NOESY 核磁共振谱图。

Figure 1. (a) Chemical structures of CB-AN-PBI, CB-PH-PBI, CB-PBI and CB-AN; (b) Partial  $^{1}$ H NMR (600 MHz) spectra of CB-PBI, CB-AN-PBI, CB-AN and CB-PH-PBI in CD<sub>2</sub>Cl<sub>2</sub> at 298 K ( $c \sim 2$  mM); (c) Excerpt from a  $^{1}$ H- $^{1}$ H NOESY NMR (600 MHz) spectrum of CB-AN-PBI in CD<sub>2</sub>Cl<sub>2</sub> at 298 K ( $c \sim 2$  mM).

8

发后随溶剂极性增加而持续变化的激发态动力学过程。基于跨空间电荷转移对微环境极性的独特敏感性,该薄膜对烷烃气体的存在表现出快速(~5 s)、灵敏(~10 ppm)和选择性响应。据此,我们创制了一种概念性薄膜荧光传感器。该传感器体积小(~3.7 cm³)、能耗低,可在常温下工作。由此实现了对饱和烷烃的原位在线监测,有望满足实际探测需要。

功能分子的 U 形非平面结 构有效避免了芳烃单元的紧密堆 积,保证了传感过程的高效传质。 此外,跨空间电荷转移这一发光 本质使得薄膜对微环境改变异常 敏感,由此保障了敏感薄膜的高 性能。这一实践为荧光传感单元 的的理性设计提供了新的思路。

第一作者: 陕西师范大学王朝龙博士通讯作者: 陕西师范大学房喻院士全文链接: https://doi.org/10.1002/anie.202207619

Alkanes are widely used as fuels, important industrial crude materials and chemical solvents in modern-day society. Alkane vapor is highly flammable and explosive when it exceeds a certain concentration, a potential danger to public safety. In addition, alkane vapors such as n-pentane and n-heptane are taken as bio-markers

in exhaled breath samples of lung cancer patients in volatolomics. Therefore, their sensitive detection is of great significance to environmental and occupational safety as well as point-of-care diagnostics. Considering the volatility and chemical inertness of alkanes, detecting them could be challenging especially at trace levels, and thereby it is desirable to establish sensitive, inexpensive, quick and portable sensing method for alkane vapors to adapt to onsite and real-time gas monitoring scenarios.

Fluorescent film sensor (FFS) has attracted extensive attention in the field of fluorescent sensing owing to their unique virtues, including high speed and sensitivity, simplicity, miniaturization, reversibility as well as on-line and in situ detection. which offers a promising choice for the required vapor monitoring. As revealed, the performance of a FFS is largely determined by the following factors: 1) chemical nature of the sensing fluorophore, 2) adlayer structure of the film, 3) hardware structure of the sensor. and 4) signal processing strategy, etc. Among them, innovative design of sensing fluorophore and optimization of adlayer structure are at the core for the development of high-performance FFSs.

In this study, we report for the first time a high-performance FFS for the alkanes with a rationally designed through-space charge

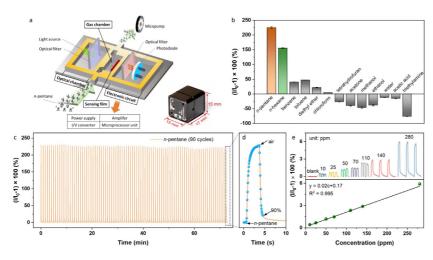


图 2. (a) 自主搭建的传感器件结构示意图; (b) 荧光传感薄膜对不同挥发性有机化合物的传感响应; (c) 荧光传感薄膜对正戊烷气体的重复性测试; (d) 荧光传感薄膜对正戊烷气体的传感动力学曲线; (e) 荧光传感薄膜对正戊烷气体的检出限测试。

Figure 2. (a) Schematic description of the sensory unit of the home-made sensing platform. Inset: photograph of the sensory unit; (b) Fluorescence responses of the CB-AN-PBI-based film sensor to n-pentane, n-hexane and various potential interferences; (c) Real-time responses of CB-AN-PBI-based film sensor to saturated n-pentane in more than 90 repeated sensing cycles at 298 K; (d) An enlarged sensing cycle for analysis of the response and recovery time; (e) Fluorescence responses of CB-AN-PBI-based film sensor to n-pentane at different vapor concentrations.

transfer (TSCT) molecule as the sensing fluorophore. The specially selected donor-acceptor pair of anthryl group and perylene bisimide moiety are tethered in face-to-face alignment onto an o-carborane unit, which depicted dual-emission and prominent solvato-chromic property. Femto-second transient absorption spectroscopy revealed continuous TSCT dynamics in the excited U-shape molecule with increasing medium polarity. Harnessing the unique microenvironmental sensitivity of TSCT, the compound-based FFS showed an experimental detection limit of ~10 ppm for n-pentane, less than 5 s for a full detection, negligible interference and super-stability, elucidating the effectiveness of the design strategy. Notably, the sensor is small (~3.7 cm<sup>3</sup>), power-saving, and workable at room temperature.

Such outstanding sensing performance is mainly ascribed to the combination of the non-planar structure and the microenvironmental sensitivity of the newly designed sensing fluorophore. This work demonstrates that rational design of fluorophores possessing TSCT properties can be employed as an effective strategy to develop high-performance FFSs.

First Author: Dr. Wang Zhaolong, Shaanxi Normal University Correspondence Author: Prof. Fang Yu, Shaanxi Normal University Full Text Link: https://doi.org/10.1002/ anie.202207619



#### Journal of Colloid and Interface Science

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Interfacially confined preparation of copper Porphyrin-contained nanofilms towards High-performance Strain-Pressure monitoring

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### 基于铜卟啉纳米薄膜的高性能 应力应变传感器

研制一种超灵敏、抗干扰的 柔性应变压力传感器,将人体运动转化为电容或电阻的变化,对 老年人和患者的健康监测具有重 要意义。通过对肌肉痉挛、臂膀 摇摆和剧烈运动的准确识别,可 以实现远程在线诊断,随时随地 为患者提供医疗服务。然而,这 种应用有两个基本的传感需求, 即信号检测和动作识别。通过直 接短路和恢复传导通路来调整纳 米间隙的宽度后,纳米薄膜传感 器在现有的基于几何应变和压阻 应变响应机制的信号检测设计中 表现出超高的灵敏度。

将传感材料设计与结构工程相结合,为满足信号检测与识别的双重要求提供了广阔的前景。卟啉基共价有机框架(POFs)是一种具有超分子结构的纳米多孔材料。由于合成化学的进步,可以构建具有预期几何形

状的 POFs, 其功能部分可以集成到材料的网络中。此外,金属节点和有机配体可以作为载流子转运的位点,适当的金属离子螯合使 POFs 具有半导体性质。因此,如果连接臂较长且较软,预计 POFs 在分子水平上的孔隙率会发生变化,在施加机械应力时可以调节电荷传输能力。因此,POFs 可以看作是应变传感器的功能框架,通过沿着软 POFs 骨架的网络级联进一步放大局部变形诱导的信号,可实现对微小应变/压力的超灵敏检测。

本文报道了一种碘掺杂的铜卟啉基纳米薄膜 (I<sub>2</sub>@CuPTFA) 为传感材料的超灵敏应变压力传感器。所研制的传感器满足了对人体不同动作的连续采集和高灵敏识别。具体来说,我们观察到,在应变范围为 3-7% 时,响应灵敏度大于 10000,超过 5000 次的

动态工作循环,证明了传感器的 持久性。

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It is important for the medication of elder people and patients to develop flexible strainpressure sensors capable of translating gentle motions of living body into electric capacitance or resistance changes through ultrasensitive and anti-jamming ways. By means of accurately discriminating muscle hyper-spasm, anoetic swaying and vigorous sporting activities, it is possible to track epilepsy via remote online diagnosis in a real-time manner, so that healthcare service can be delivered to patients at any time and place. However, there are two basic sensing requirements for such applications, namely, signal detection and recognition. After the width of nanogap is adjusted by directly disrupting and recovering conducting pathways, crack sensors currently exhibit the highest sensitivity to signal detection among the existing designs based on the mechanisms of responding to geometrical and piezoresistive strains. However, the noise-screening criteria may become self-contradictory due to indiscriminative gauging of subtle vibration at the lower limit of detection ( $\varepsilon$  less than 1%), while the nano-cracks developed uncontrolledly on the entire

sensing materials can inevitably severely deteriorate the device reliability. Therefore, it is still a great challenge to develop strainpressure sensor materials that are ultrasensitive, anti-jamming, and durable.

The combination of design of advanced sensing materials with structure engineering can

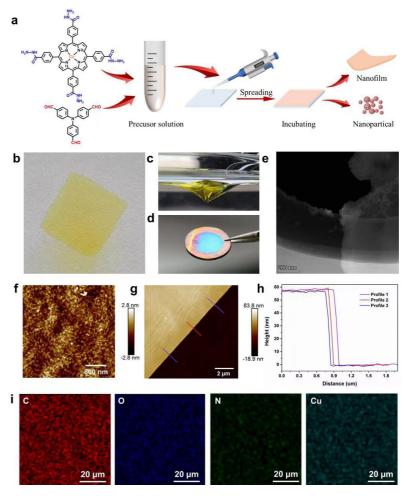


图 1. CuPTFA 纳米薄膜的制备和表征。(a) 纳米薄膜的制备过程示意图, (b) 纳米薄膜漂浮在水面上, (c) 用尖镊子按压 CuPTFA 纳米薄膜, (d) 在铜环上自支撑的 CuPTFA 纳米薄膜, (e) 以 PET 膜为基底的纳米薄膜的 SEM 图像, (f) 无支撑的纳米薄膜的表面形貌, (g) CuPTFA 纳米薄膜在硅片上的 AFM 图像, (h) g 图相对应的纳米薄膜的 AFM 高度图, (i) EDS 谱图分别描绘了 C, O, N和 Cu 元素在纳米薄膜上的分布。

Figure 1. Preparation and characterization of CuPTFA-based nanofilms. (a) Schematic representation of the preparation process, (b) a piece of nanofilm floating on water surface, (c) CuPTFA-based nanofilm pressed with thin-tipped tweezers, (d) a piece of self-standing CuPTFA-based nanofilm supported by a copper ring, (e) SEM image of the nanofilm with PET membrane as the substrate, (f) surface morphology of the free standing nanofilm, (g) a representative AFM image of the CuPTFA-based nanofilms on silicon wafers, (h) AFM height profiles of the nanofilm corresponding to the lines depicted in 'g', and (i) EDS spectrum mappings depicting, respectively, the elemental distributions of C, O, N and Cu in the examined nanofilm.

provide promising opportunities for satisfying the requirements for both signal detection and recognition. Porphyrin-based covalent organic frameworks (POFs) are nanoporous materials possessing clear supramolecular structures. Thanks to progress in synthetic chemistry, the POFs with anticipated geometries can be built, and predesigned functional moieties can be integrated into the networks of the materials. Moreover, chelation of suitable metal ions can endow the POFs with a semiconducting property as the metallic nodes and organic ligands can be taken as the sites of charge carrier transport. Therefore, it is anticipated that the porosities of POFs at the molecular level will be changeable if the linkers are long and soft, so the charge transport capability can be modulated when mechanical stress is applied. As a result, the POFs can be regarded as molecular analogs of crackbased strain sensors, and signals induced by local deformation can be further amplified through cascading of networks along the soft POFs skeleton, so as to realize ultrasensitive detection of tiny strain/pressure.

An ultrasensitive strainpressure sensor with iodine-doped
Cuporphyrin framework-based
nanofilms (I<sub>2</sub>@CuPTFA) as the
sensing materials was reported in
this study. The sensor developed
fulfilled the ultrasensitive and antijamming criteria for continuous
collection and discrimination

of different human motions. Specifically, it was observed that the gauge factor was greater than 10,000 at a strain level of 7%, and the durability was achieved after over 5000 dynamic operating cycles in the strain range of 3-7%. Remarkably, the out-of-scale strain was effectively released by integrating the I<sub>2</sub>@CuPTFA nanofilm into a sandwich-like

vertical device of Au/Nanofilm/Au, thus causing non-responsiveness at strain levels below 3% and above 7%, and recognizing different human body motions.

First author: Tang Jiaqi, PhD candidate, Shaanxi Normal University Correspondence Authors: Prof. Fang Yu, Shaanxi Normal University, Prof. Chuan Zhao, University of New South Wales Full text link: https://doi.org/10.1016/ j.jcis.2022.01.007

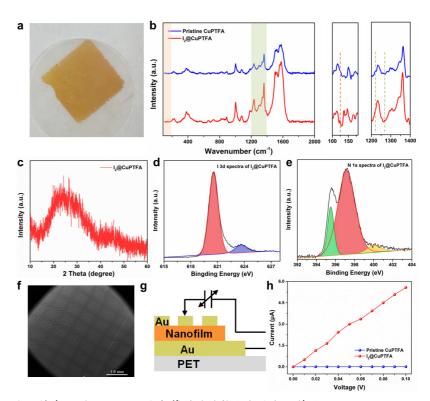


图 2. 掺杂  $I_2$  的 CuPTFA 纳米薄膜的结构和电流电压特性。(a)  $I_2$ @CuPTFA 纳米薄膜的照片,(b) 原始和碘掺杂的 CuPTFA 纳米薄膜的拉曼光谱 ( $I_2$ @CuPTFA),(c)  $I_2$ @CuPTFA 纳米薄膜的 X 射线轨迹,(d, e) 分别为  $I_2$ @CuPTFA 纳米薄膜的核级 I 3d 和 N 1s 的 X 射线光电子能谱 (XPS),(f, g) 以 PET 为衬底的 Au/I2@CuPTFA/Au 的结构和示意图,(h) 原始纳米膜和掺杂碘纳米膜的电流电压特性。

Figure 2. Structure and current–voltage property of the CuPTFA-based nanofilm doped with  $I_2$ . (a) A photo of a piece of representative  $I_2$ @CuPTFA nanofilm, (b) Raman spectra of a pristine and an iodine doped CuPTFA-based nanofilms ( $I_2$ @CuPTFA), (c) X-ray trace of the  $I_2$ @CuPTFA nanofilm, (d, e) core-level I 3d and N 1s X-ray photoelectron spectrua (XPS) of the  $I_2$ @CuPTFA nanofilm, respectively, (f, g) a picture and schematic llustration of the structure of Au/ $I_2$ @CuPTFA/Au, where PET was employed as substrate, (h) current–voltage characteristics of the pristine nanofilm and the iodine doped nanofilm.



A triphenylamine-based Pt(II) metallacage *via* coordination-driven self-assembly for nonlinear optical power limiting †



Zihao Yin, <sup>a</sup> Xingmao Chang, <sup>a</sup> Jianyang Zang, <sup>a</sup> Simin Lin, <sup>a</sup> Zhijie Zhou, <sup>a</sup> Taihong Liu, <sup>b</sup> <sup>a</sup> Liping Ding, <sup>b</sup> <sup>a</sup> Haonan Peng <sup>b</sup> <sup>a</sup> and Yu Fang <sup>b</sup> <sup>a</sup>

#### 三苯胺基 Pt(II) 超分子配位笼的组装及其 光限幅应用

光限幅材料是指在激光能量较低时具有较高的非线性透过率,而随着入射能量的不断增加,非线性透过率不断降低的材料。 因此该材料能够有效将激光的输出功率限制在一定范围内,从而达到对人眼及敏感光学器件的保护。目前,基于双光子吸收机理的有机光限幅材料已得到了飞速发展,但纯有机材料往往光稳定 性较差,因此具有更高光化学稳定性的有机 - 无机杂化材料受到了广泛关注。

超分子配位复合物(SCCs) 是由金属节点及有机配体通过配 位驱动自组装得到的超分子组装 体,具有结构明确、光物理性质 丰富、溶解性好等优点。在组装 中引入具有双光子吸收性质的有 机配体可以赋予 SCCs 双光子特 性,并有望应用于光限幅、细胞 成像等领域。

本工作以具有八极结构的三苯胺基吡啶配体为核心荧光单元,通过与90°Pt及对苯二羧酸进行超分子配位自组装得到了具有扭曲三棱柱结构的新型3D金属笼;通过核磁、质谱及单晶解析确认了金属笼的结构。单光子光物理性质的研究表明,金属

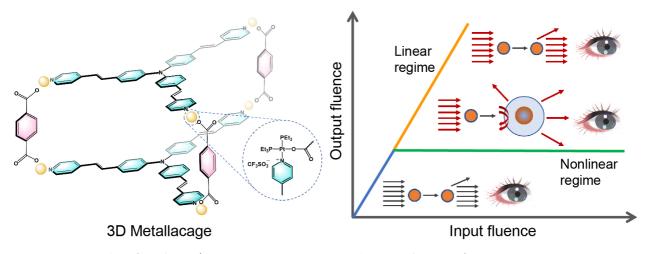


图 1. 超分子配位自组装得到的具有扭曲三棱柱结构的新型 3D 金属笼及其光限幅特性 Figure 1. Chemical structure of the triphenylamine-based metallacage via coordination-driven self-assembly and its optical power limiting property

笼的最大发射波长在 600 nm,最 大吸收波长在 440 nm,相对于相 应的三苯胺基配体均发生了明显 红移,因此可以有效增加穿透深 度。此外,金属笼在 750 nm 激 光激发下的最大双光子吸收截面 值(δ 2PA)可达 2010 GM,为 配体的 2.4 倍,证明配位作用实 现了 1+1>2 的效果。此外,金属 笼的光限幅性能远优于配体,且 具有更加优异的光稳定性,因此 用于未来光限幅器件的构筑。

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Optical limiting materials are the materials with high nonlinear transmittance under low laser energy intensity, while the transmittance decreases with the increase of the input intensity, so that these materials could limit the output energy within a certain range, which could protect the human eyes and sensitive optical devices. At present, organic optical limiting materials based on twophoton absorption mechanism have been developed rapidly, while pure organic materials always have poor photo-stability, therefore the organic-inorganic hybrid materials have attracted more attention.

Supramolecular coordination complexes (SCCs) are supramolecular assemblies synthesized by coordination-driven self-assembly using metal nodes

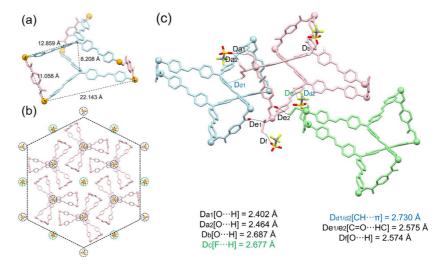


图 2. 三苯胺基 Pt(Ⅱ) 超分子配位笼的单晶结构 Figure 2. Solid-state superstructure of the metallacage obtained from singlecrystal X-ray crystallography

and organic ligands, which have unique advantages due to their well-defined structure, abundant photophysical properties and good solubility. The introduction of organic ligands with two-photon absorption properties can endow SCCs with two-photon characteristics, which can be applied in the field of optical limiting, biomedicine and cell imaging.

In this work, we chose the triphenylamine-based pyridine ligand as core fluorescence unit, and obtained a novel 3D metallacage with a twisted triangular prism structure via coordination-driven self-assembly by the ligand, 90° Pt and 1,4-dicarboxybenzene. The structure of the metallacage was fully characterized by NMR and ESI-TOF-MS and single-crystal X-ray diffraction. The one-photon photophysical properties

investigation revealed that the metallacage showed an apparent red-shifted luminescence centered at 600 nm and absorption centered at 440 nm compared with the constituent triphenylamine-based ligand, which was capable of increasing penetration depth. Intriguingly, the  $\delta$ 2PA under 750 nm laser irradiation can reach 2010 GM, which is about 2.4fold of the ligand. This 1+1>2 phenomenon could be attributed to the coordination effect. Moreover, the optical limiting performance of the metallacage is much better than that of the ligand, and the metallacage also presents excellent photo-stability, making it a potential candidate for the construction of future optical limiting devices.

First Author: Master's candidate Yin Zihao, Shaanxi Normal University Correspondence Author: Assoc. Prof. Peng Haonan, Shaanxi Normal University Full-Text Link: https://pubs.rsc.org/en/content/ articlelanding/2022/tc/d2te01256a

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#### Insight into the Clustering-Triggered Emission and Aggregation-Induced Emission Exhibited by an Adamantane-Based Molecular System

Wenjun Xu, Dingfang Hu, Zhaolong Wang, Gang Wang, Ke Liu, Jingjing Liang, Rong Miao\*, and Yu Fang\*

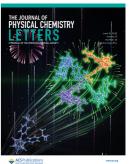
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### 基于金刚烷分子体系深入理解 簇发光和聚集诱导发光现象

随着对荧光科学技术的长 期、系统、深入的研究, 衍生出 旨在研究微观分子与宏观物质 之间的聚集科学。其中,聚集 诱导发光 (Aggregation-Induced Emission, AIE)由于聚集态强 荧光使其发光变化易于跟踪观 察,成为了研究聚集科学的理想 选择。目前广泛接受的 AIE 机制 是聚集态分子运动受限以及激发 态 π 扭曲导致的最小能量圆锥 交点(MECI)。基于这一理论, 可以理解许多不同寻常的发光现 象,如结晶诱导发射(CIE)、 聚集诱导延迟荧光(AIDF)等。 此外,一些自然界的生物大分子 (如纤维素和蛋白质)、天然和 合成聚合物等虽然不具有共轭 结构,但在紫外光照射下也能 发出可见光,这一类发光被称 为簇发光(Clustering-Triggered Emission, CTE)。虽然已有的 研究将 CTE 机制归因于跨空间电

荷转移(TSCT),但是其研究大 多基于聚合物体系,对 CTE 小分 子缺乏系统研究。因此,对具有 确定分子结构和结晶结构的聚集 可控的小分子体系进行系统的探 索,不仅有助于深入理解已报道 的发光现象,尤其是 CTE 的发射 机制,而且有助于揭开聚集科学 的神秘面纱。

本工作中,我们报道了具有 CTE 和 AIE 性质的小分子体系(Ad-4CP),其中四个邻碳硼烷衍生物(Cb-Ph)分别连接在金刚烷的四个仲碳原子上。因此,Ad-4CP分子可以看作是四个 Cb-Ph 分子单元化学团簇的结果。令人惊讶的是,Cb-Ph 在溶液和聚集态下均不发光,而 Ad-4CP 在溶液中发出明显的荧光,并且聚集态荧光显著增强。随着系统深入的研究,Ad-4CP 在溶液态的双发射分别属于局域激发(LE)态和分子内电荷转移

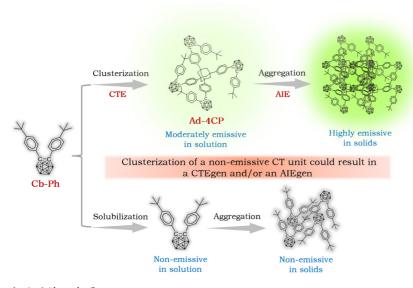
(ICT)态。同时,Ad-4CP是优良的 AIE 分子,在固态下荧光量子产率大于 0.5,其发射来自于分子内和分子间的电荷转移相互作用,并因此呈现出显著的激发波长依赖发射(荧光从绿色到黄色)。本工作不仅设计了一个具有 CTE 和 AIE 特性的特殊小分子体系,而且通过合适结构单元的簇集,为 CTE 和 AIE 分子体系的合理设计提供了有价值的见解。

本研究插图被选为当期杂志 封面予以推介。

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Long term, systematic and in-depth study of aggregation-related luminescent science and technology enabled the birth of Aggregate Science aimed to deal with the phenomena in between microscopic molecules and macroscopic substances.



分子设计示意图 Schematic illustration of the designed molecular clusterization-induced fluorescence

To explore the intrinsic science, aggregation induced emission (AIE) is ideal because luminescent changes are easier to follow in both dissolved and aggregated states. The widely accepted AIE mechanism is the restriction of intramolecular motion (RIM) in the aggregated state and the  $\pi$  twisting and distortion in the excited state that result in minimum energy conical intersection (MECI). Based on the rationalization of RIM and  $\pi$ twisting, fluorescence phenomena of many unusual molecular systems can be understood, such as crystallization-induced emission (CIE), aggregation-induced delayed fluorescence (AIDF), and so on. In addition, some naturally found fluorescence from biomolecules (such as cellulose and protein) and polymers (natural and synthetic polymers) can emit visible light

under UV irradiation, though they do not have large conjugated structures, which is defined as clustering-triggered emission (CTE). Although reasonable explanations, through space charge transfer (TSCT), have been proposed for the origin of CTE, a well-recognized explanation for small CTE molecular systems is absent. Therefore, detailed exploration of CTE related small aggregation-controllable molecular systems not only favors in-depth understanding of the reported bioluminescence, but also contributes to unravel the mysteries behind Aggregate Science.

Herein, we report a molecular system with both CTE and AIE properties, where four non-emissive o-carboranyl derivatives of benzene (Cb-Ph) were attached, respectively, to the four tertiary

carbon atoms of adamantane (Ad-4CP). Hence, Ad-4CP can be taken as a result of chemical clusterization of four Cb-Ph units. Surprisingly, Cb-Ph is neither emissive in solution nor in aggregated state, but Ad-4CP emits obvious fluorescence in solution and greatly enhanced fluorescence upon aggregation. Further studies revealed that the two emissions in solution were ascribed to the locally excited (LE) state and intramolecular charge transfer (CT) state, respectively. And Ad-4CP is a favorable AlEgen with an emission efficiency greater than 0.5 in solid state, where the emission could originate from both intraand inter-molecular CT interaction of Ad-4CP. Owing to the two-level CT interaction, Ad-4CP crystal depicted remarkable excitation dependent emission (from green to yellow). We believe that the present work not only delivers a peculiar molecular system with both CTE and AIE properties, but also provides valuable insights on molecular engineering for rational design of CTE and AIE systems via clusterization of suitable structural units.

The illustration of this work is featured on JPCL cover.

First Author: Xu Wenjun, doctoral candidate at Shaanxi Normal University Correspondence Authors: Prof. Fang Yu, Assoc. Prof. Miao Rong, Shaanxi Normal University Full Text Link: https://pubs.acs.org/

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#### Rigid Bay-Conjugated Perylene Bisimide Rotors: Solvent-Induced Excited-State Symmetry Breaking and Resonance-Enhanced Two-Photon Absorption

Wan Feng, Qingwei Jiang, Zhaolong Wang, Jianyang Zang, Gang Wang, Ke Liu, Haonan Peng, Taihong Liu\*, Liping Ding, and Yu Fang\*

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#### Chemistry B

#### 湾位修饰苝二酰亚胺衍生物的溶剂诱导激发态 对称性破缺和共振增强双光子吸收效应研究

分子内电荷转移和激发态对 称性破缺在多偶极荧光化合物的 非线性光学领域中扮演着重要角 色。本工作系统考察了非平面碳 硼烷湾位功能化的菲二酰亚胺结 构衍生物(PBIs)光物理性质, 其在极性溶剂中 A<sub>0-0</sub>/A<sub>0-1</sub> 比值明 显下降, 二聚体荧光发射峰消失, 表明在该共轭体系中,相邻 PBI 单元因 π-π 堆积而产生了强激 子耦合作用。基于不同长度炔键 连接臂的自由旋转特性, 在弱极 性溶剂中, 共轭桥弱耦合相连的 二个相同 PBI 基团之间形成的二 聚体在一定条件下可以发生超快 的电荷分离现象。具体分析而言, 当其中一个 PBI 片段被激发后, 与另一个处在基态下的 PBI 片段 相互作用,导致分子对称性破坏 电荷分离(SBCS)发生电子分离

形成阳离子与阴离子自由基,飞 秒时间分辨瞬态吸收光谱吸收证 实了花二酰亚胺阴离子(PBI-) 和阳离子(PBI+)自由基产生, 该类衍生物弛豫动力学明显差异 从微观动力学的角度证实了可能 的激发态对称性破缺现象。

另外, 基于湾位修饰和共振 增强机制的协同作用,该系列衍 生物较之常规 PBI 衍生物,最大

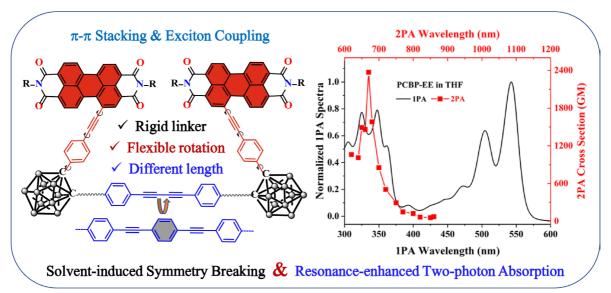


图 1. 衍生物的化学结构式及其双光子吸收性能

Figure 1. Chemical structures of multipolar molecular rotors and related 2PA properties

双光子吸收波长红移至 670 nm。 同时,化合物在极性溶剂中的双 光子吸收截面值明显增加,这表 明了对称性破缺引起的分子内电 荷转移程度增强。

该工作表明具有刚性可旋转 构型的衍生物中相邻的 PBI 单元因 π-π 堆积而产生了强激子耦合作 用,溶剂诱导产生激发态对称性 破缺与电子给体与受体的电子耦 合强度、生色团之间的距离以及 反应物与周围溶剂环境密切相关。 同时利用共轭分子的激发态分子 结构变化和环境效应控制电荷分 离速率和共振增强效应显著改变 化合物的双光子吸收特性。

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Intramolecular charge transfer and excited-state symmetry breaking have significant effect on the nonlinear optical properties of multipolar chromophores. Rigid and nonplanar perylene bisimide derivatives (PBIs) functionalized at bay-positions were comparatively and comprehensively investigated. In apolar solvents, two quadrupolar molecular rotors showed an obvious decrease of the A<sub>0-0</sub>/A<sub>0-1</sub> ratios, suggesting strong exciton coupling with the adjacent PBI units initiated by the  $\pi$ - $\pi$  stacking. The vanishment of the preferable dimer emission in polar solvents

dimer emission in polar solvents supported the plausible phenomena of excited-state symmetry breaking thanks to the facile rotation round the rigid linkers. Comparative femtosecond transition absorption studies confirmed their notable differences in relaxation dynamics and the generation of radical anion (PBI<sup>--</sup>) and cation (PBI<sup>-+</sup>).

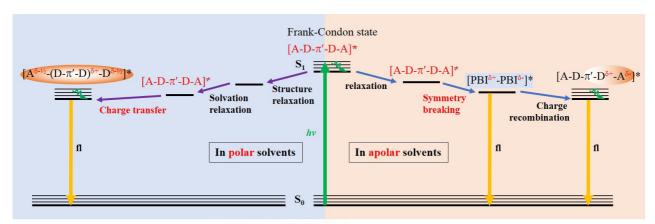
The maxima two-photon absorption (2PA) wavelengths obtained for the molecular rotors were slightly red-shifted to 670 nm with intrinsic resonance-enhanced characteristics, reflecting the synergistic effect of functional positions and molecular architectures.

Meanwhile, the obvious increase of significant 2PA cross sections values in polar solvents illustrated the stabilization of the symmetry broken dipolar states. Further femtosecond Z-scan also manifested the contribution of excited states dynamics on the nonlinear optical properties of the multipolar chromophores.

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PCBP-EE or PCBP-EPE (A-D- $\pi'$ -D-A)

图 2. 湾位修饰花二酰亚胺衍生物的溶剂诱导激发态对称性破缺光物理过程示意图

Figure 2. Schematic diagrams of photo excitation, excited-state symmetry breaking charge transfer, and emission processes of superior PBIs depending on the environmental polarity.

#### 交流合作 Exchange and Cooperation



#### 陕西省科技厅赵怀斌副厅长一行参观考察

## Shaanxi S&T Dept vice director Zhao Huaibin visits Surface Chemistry Center

6月14日上午,省委科技工委 委员、省科技厅副厅长赵怀斌一行 参观调研光子鼻与分子材料研究团 队和陕西省基础学科(表界面化学) 研究中心。副校长董治宝、科技处 处长唐三一以及学校职能部门部分 人员陪同参观调研。

房喻院士向赵怀斌副厅长一 行概括介绍了团队科研历程以及 从基础研究到产业应用方面取得 的重要成绩,具体从荧光传感器 技术到叠层式传感器结构、再到高端 SRED 系列便携式爆炸物/毒品检测仪的诞生,薄膜基荧光传感器技术打破了国外公司对传感器技术的垄断,实现了从并跑到领跑的技术突破。同时房喻院士介绍了凝胶化学在凝胶推进剂、高能量密度含能材料、软模板基轻质高强聚苯乙烯泡沫材料(STPS)等领域的重要技术应用,并展望了团队研发的新技术和新

材料的推广和应用。

赵怀斌副厅长肯定了团队在 基础研究方面取得的成绩,同时 推介了秦创原创新驱动平台,希 望加快促进优秀科技成果在陕西 落地转化。

On June 14, Mr. Zhao Huaibin, member of Committee on Science and Technology of CPC Shaanxi Provincial Committee and vice director of Shaanxi Provincial Department of Science and

#### 交流合作 Exchange and Cooperation

Technology, visited the Photonic Nose and Molecular Materials group and Shaanxi Provincial Basic Discipline Research Center for Surface Chemistry at Shaanxi Normal University.

SNNU vice president Dong Zhibao, Department of Science and Technology director Tang Sanyi and other officials accompanied the visit.

Prof. Fang Yu briefed Zhao Huaibin and his associates about his group's research progress and major achievements from basic research to industrial application, evolving from fluorescent sensors technology to laminated sensor structure, to high-end SRED series portable explosives and narcotics detectors, particularly the thin film fluorescent sensors which broke the monopoly of foreign companies on sensor technologies and realized a technological breakthrough of taking the lead instead of running together. Fang also briefed about applications of the group's work in gel chemistry in gelled propellant, high-energy density energetic material, and light-weight highstrength Soft Template-based Polystyrene Foam (STPS), and envisioned the promotion and industrialization of the group's new technologies and new materials.

Zhao Huaibin affirmed Fang group's research achievements, recommended Shaanxi province's Qinchuangyuan Innovation Platform, and hoped more outstanding scientific and technological achievements could be industrialized in Shaanxi.

### 计算机科学学院马苗教授 受邀进行学术交流

School of Computer Science's Ma Miao invited to share her research



On June
14, Prof.
Ma Miao of
Shaanxi Normal
University's
School of
Computer
Science was
invited to share
her research at
the lecture hall

为推进学科交叉融合,营造良好的学术分享交流氛围,团队于6月14日下午邀请我校计算机科学学院马苗教授在致知楼1668会议室进行学术交流。团队全体教师、物理学与信息技术学院辛云宏教授和团队部分研究生参加了交流会。会议由刘静教授主持。

马苗教授首先介绍了自己的 研究领域和研究专长,随后系统 介绍了 AI+ 教育,群体感知、灰 色理论、群体智能优化算法等图 像处理关键技术,以及深度神经 网络模型在数据处理中的应用和 探索。

团队师生就小波变换、灰色理 论等内容与马苗教授进行了深入交 流和讨论。 in Zhizhi Building.

The event was attended by teachers and students of the Fang group and Prof. Xin Yunhong of School of Physics and Information Technology.

Ma Miao first introduced her research area and specialties, then presented her research and insights in AI + education, image processing key technologies such as crowd perception, grey theory and swarm intelligent algorithm, and exploration and application of deep neural network model in data processing.

At the end of the report, Ma
Miao also answered questions from
the audience and they had an indepth discussion in topics such as
wavelet transformation and grey
theory.

#### 心绪感悟 Thoughts and Reflections

#### 留法行前感言 Words Before I Leave to Study in France

文/万岳瞻 Wan Yuezhan

这时光总像林花谢了春红, 却只叹,脚步太匆匆。转眼硕士 三年已近尾声,多少离愁别绪情, 不觉间,涌上心头。

"彭彭家"这个略显调皮与 腻歪的称谓是我对致知楼 1606 实验室最真挚的记忆,导师彭军 霞老师如父如母般的呵护与教 导,让这份情谊更加厚重无比。 细数我与导师初相识,是在她的 办公室,她教导我要多与人交流, 要学会合作,如今每每想起,仍 然是那般语重心长。

生活上,老师经常挂在嘴边的叮嘱就是,好好吃饭,疫情期间千万做好个人防护,但就是这平平淡淡的一句,总能让我们感受到家的温暖。

学习上,老师对我们要求严格,不管从实验设计、实验操作,还是结果分析,老师总是亲力亲为,手把手指导我们。印象最深刻的就是刚进实验室做合成实验,老师说我点板的方式不对,非常耐心的教我点板。还有第一次做扫描电镜时,老师亲手教我制样。如今回忆起来,这些瞬间依然历历在目。

在此, 感谢恩师对我的教

导,您永远是我学术生涯上的领路人,真诚祝愿您身体健康,工作顺利,家庭幸福。同时,也祝愿旭旭和琪琪两位小师弟开开心心,健康成长。

很幸运,我今年申请 CSC 去 法国图卢兹大学攻读博士学位的 项目,前几天也收到了录取信。 在此,感谢恩师在申请期间对我 的全力帮助,感谢陕西师范大学 这个平台,感谢教育部和留学 基金委的信任,更要感谢 Fang Group 各位老师的无私帮助,各 位小伙伴的三年陪伴。最后,再 次祝贺房老师成功当选中国科学 院院士,能做为您的学生,我深 感荣幸。

How time flies. It was like just a blink of the eye, yet it is almost the end of my three years' study as a master's candidate. For a moment, I was too immersed in parting sentiment to bid farewell.

The "PengPeng's" --- this somewhat naughty and intimate term always brings me back to the lab 1606 in Zhizhi Building. The parent-like care, support and instruction from my advisor Ms Peng Junxia made the memories even dearer. When I first met her in her office, she told me to



communicate more and learn to cooperate with others. I can still feel the sincerity and earnest when I learned the importance of this later on.

In life, she often remind us to eat on time and be careful with self-protection during the COVID-19 pandemic, which makes us feel the warmth of home.

In research, she is always strict with us, teaching us in every step from experiment design, experiment operation to result analysis in a hands-on approach. What impressed me most is that she told me I run the TLC plate incorrectly and showed me the right procedures, when I did the synthesis experiment for the first

#### 心绪感悟 Thoughts and Reflections

time. At another time, she showed me how to make a sample with the scanning electron microscope. These moments are still vivid in my mind when I recall them now.

I would like to take this opportunity to thank Ms Peng for her guidance and you are always the guiding star on my career path. I sincerely wish you good health, successful work and happy family. In the meanwhile, I would like to wish happiness and health to my junior fellow students Xuxu and Qiqi.

I am fortunate that my application for a Chinese Scholarship Council-sponsored PhD program at University of Toulouse, France has been approved. My thanks go to Ms
Peng, my alma mater, MOE and
CSC, Fang group teachers and my
fellow schoolmates for their help,
trust, support and companionship.
Last but not the least, allow me
to congratulate Prof. Fang Yu
again for being elected a CAS
academician. I am so privileged to
be one of your students.





