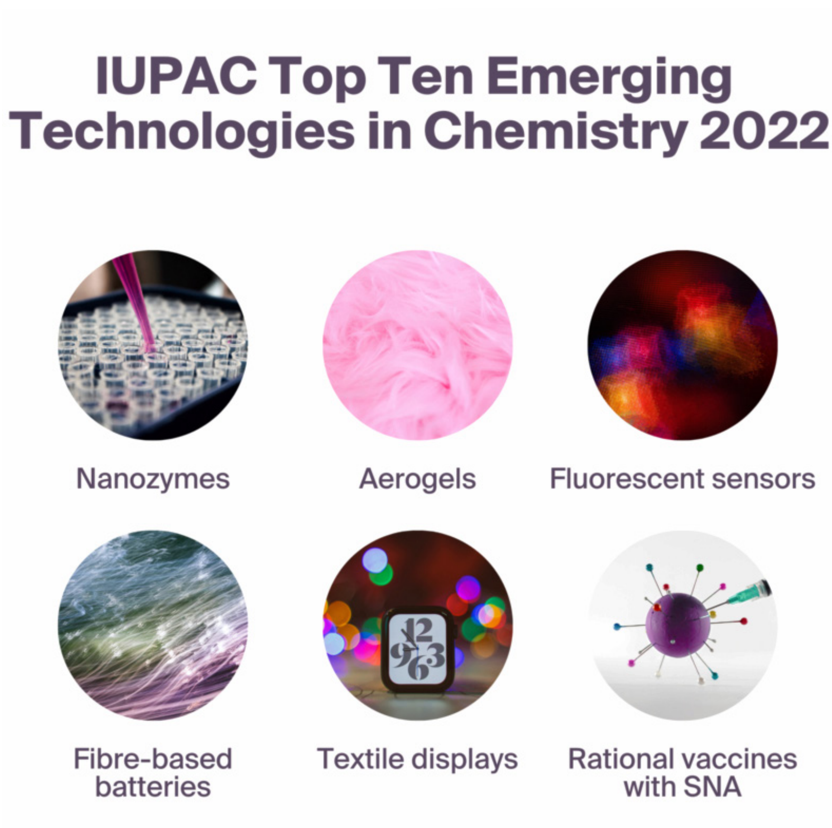
光子鼻与分子材料团队简报

Newsletter of Photonic Nose and Molecular Materials Group

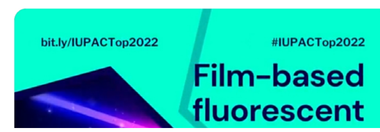
10 / 2022



IUPAC
@IUPAC

A “chemical nose” with film-based fluorescent sensors smells contaminants with high sensitivity. Other devices detect pathogens like Listeria, suggesting these fluorescent films could find uses in environmental remediation and food safety. #IUPACTop2022 buff.ly/3eOB27d

翻译推文



IUPAC
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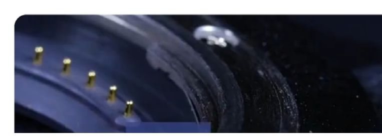
Film-based fluorescent sensors have become a widespread tool, thanks to their tuneability and versatility. Immobilised on suitable surfaces, fluorescent molecules find applications in the detection of species like NOx and VOCs. #IUPACTop2022 buff.ly/3TzOgUe

翻译推文



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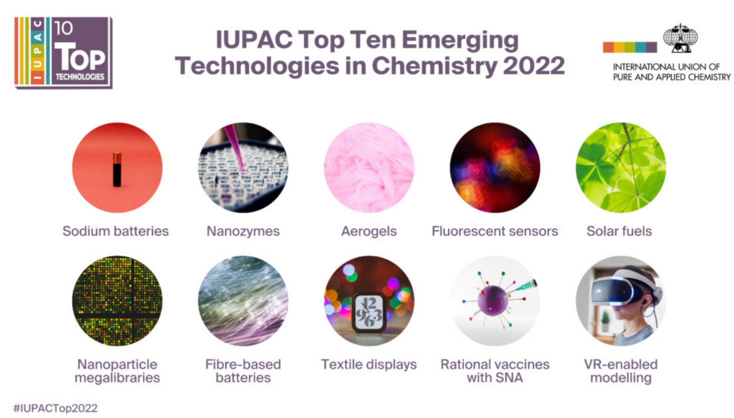
房喻院士团队薄膜荧光传感器入选 2022 化学十大新兴技术

Film-based fluorescence sensors selected among 2022 Top 10 emerging technologies in chemistry

10 月 17 日，国际纯粹与应用化学联合会（IUPAC）公布了 2022 年化学领域十大新兴技术，基于房喻院士团队研究的薄膜荧光传感器入选。



薄膜荧光传感因其优异的灵敏度、选择性、可调性与普适性等特征被认为是继离子迁移谱之后最具发展潜力的微痕量物质探测技术。在对应的器件中，具有荧光活性的分子通常被固定于尺寸可小至 1 厘米以下合适基质上，形成具有对外界刺激快速可逆响应的 2D 或 3D 薄膜材料，发挥着对微痕量物质的高效探测功能。该类荧光传感器具有尺寸小、功耗低和操作简单等优点，在便携式传感器的创制方面具有突出优势。

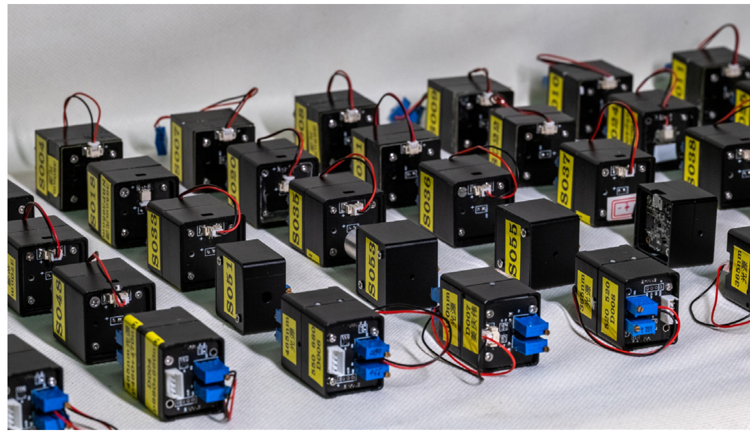
自 1998 年以来，房喻院士团队立足国家安全的重大需求，针对荧光传感技术中薄膜荧光传感易受环境因素干扰，选择性和灵敏度等难以满足特殊检测需要等诸多难题，开展了系列深入、全面的研究工作。先后提出了“激发态微环境效应”“连接臂层屏蔽 / 富集效应”，以及“侧链构象效应”等概念，发展了化学组装、凝胶介导、组合设计和界面限域动态聚合等薄膜制备策略，通过自主搭建系统，获得了含时传感信息，并将其用于复杂样品的区分检测，实现了传感性能、传感机理和薄膜制备研究的新跨越。

迄今为止，房喻院士团队发展了可高效检测 TNT、氨类化合物、氮氧化物、有机挥发物、杀虫剂、神经毒剂、尼古丁、病原体等在内的系列薄膜荧光传感器，创造了迄今响应速度最快、灵敏度最高的爆炸物与毒品类薄膜荧光探测记录。研制了具有完全自主知识产权的 SRED 系列隐藏爆炸物和毒品荧光传感器和探测装备，孵化了深圳砺剑防卫技术有限公司，专事薄膜荧光传感器的工业研发、生产和销售。相关产品在十九大、G20 峰会、博鳌论坛、首长专列、中央军委、乌干达总统府、大兴机场、深圳地铁等重大活动、重要场所安保中发挥了重要作用，2019 年开始列装部队。房喻院士团队首创的毒品薄膜荧光传感器和探测装备也开始获得应用。涉及化学战剂、神经毒剂、病原体等高危物质超灵敏探测的薄膜荧光传感器和装备研制也在有序推进中。

此次公布的十大新兴技术为

钠离子电池、纳米酶、气凝胶、薄膜荧光传感器、巨型纳米粒子图书馆、纤维电池、液体太阳能燃料、织物显示、SNA 疫苗和 VR 互动式建模，被视为是介于基础科研发现与已商业化的技术之间的革命性创新，具有为化学研究、可持续发展和其他很多方面打开新局面的巨大潜力。

国际纯粹与应用化学联合会（IUPAC）成立于 1918 年，前身为国际应用化学大会，其宗旨为解决全球关注的化学学科相关问题。其广为认知的代表性工作为统一规范化学元素及其化合物的命名标准，对元素命名和符号有最终决定权。



部分基于叠层结构的薄膜荧光传感器
Laminated film-based fluorescence sensors

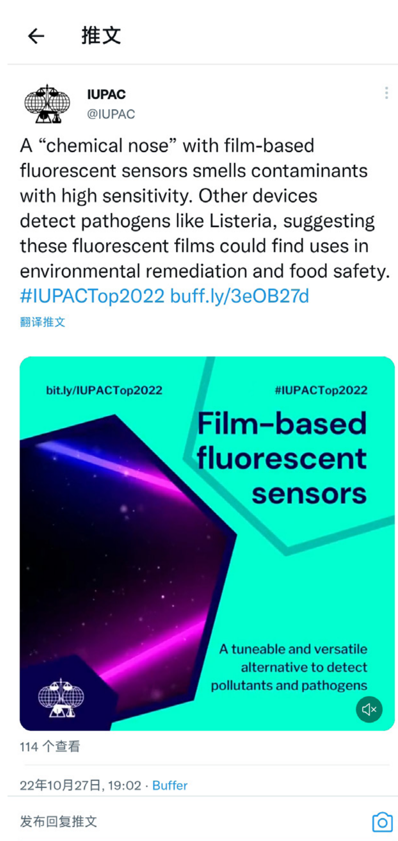
爆炸物与毒品便携式检测装置
Portable detection devices for explosives and narcotics

On October 17, the International Union of Pure and Applied Chemistry (IUPAC) released the 2022 Top Ten Emerging Technologies in Chemistry, and the film-based fluorescence sensors based on the research of Prof. Fang Yu's group was selected among the top ten emerging technologies.

Film-based fluorescence sensing is considered to be the most promising microtrace material detection technology after ion mobility spectroscopy due to its excellent sensitivity, selectivity, tunability and universality. In the corresponding devices, fluorescently active molecules are usually immobilised on a suitable surfaces that can be as small as under one centimetre in size to form 2D or 3D films with a rapid reversible response to external stimuli, which plays an efficient detection function for microtrace substances. This type of fluorescent sensors have the advantages of small size, low power consumption and simple operation, and has an outstanding advantage in the miniaturization of portable sensors.

Since 1998, based on the major needs of national security, Prof. Fang Yu's group has carried out a series of in-depth and comprehensive research work on the difficulties of film-based fluorescence sensing technology, such as being easily disturbed by environmental factors, unsatisfactory selectivity and sensitivity in meeting special detection needs. They proposed the concepts of excited state micro-environmental effect, shielding/enrichment effect of connecting arm layer, and sidechain conformation effect, and developed film preparation strategies such as chemical assembly, gel-mediated, combinational design and dynamic polymerization of interface confinement, and obtained time-containing sensing information through independent construction of the system, and used it for the discrimination and detection of complex samples, realizing a new leap in sensing performance, sensing mechanism and film preparation.

So far, they have developed a series of film-based fluorescence sensors that can efficiently detect TNT, ammonia compounds, nitrogen oxides, organic volatiles, pesticides, nerve agents, nicotine, pathogens, etc., creating the fastest response and the most sensitive film fluorescence detection record of explosives and drugs. They developed the SRED series hidden explosives and narcotics fluorescent sensors and detection equipment with completely independent intellectual property rights, and incubated Shenzhen SRED Security and Surveillance Technology Co., Ltd., specializing in the industrial research, and development, production and sale of film-based fluorescent sensors. The related products have been used in the security of major events and important venues such as the CPC 19th National Congress, G20 Summit, Boao Forum, top official's train, Central Military Commission, Uganda Presidential Office, Daxing Airport, Shenzhen Metro, etc., and began to be deployed by the military in 2019. The film-based fluorescent sensor and detection equipment for narcotics pioneered by them have also begun to be applied. The development of film-based fluorescent sensors and equipment involving ultra-sensitive detection of high-risk substances such as chemical warfare agents, nerve agents and pathogens is also in progress.



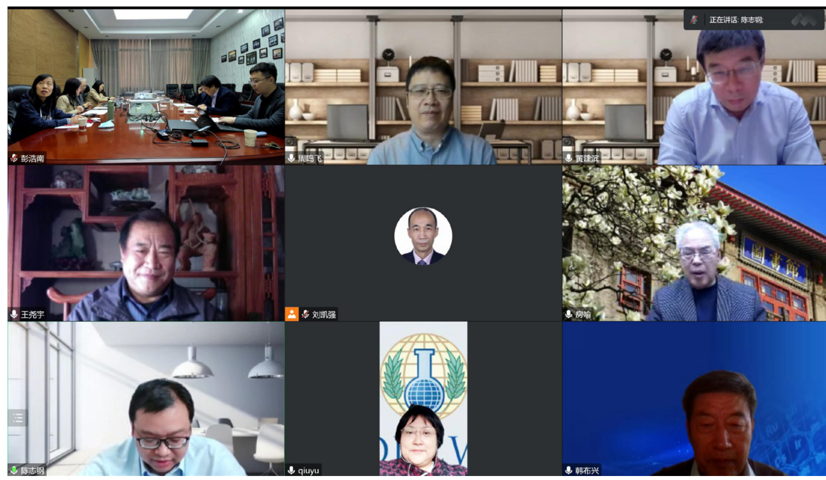
The top ten emerging technologies announced are sodium-ion batteries, nanozymes, aerogels, film-based fluorescence sensors, nanoparticle mega libraries, fiber-based batteries, liquid solar fuel synthesis, textile displays, rational vaccines with SNA and VR-enabled interactive modeling. These technologies are defined as transformative innovations in between a discovery and a fully-commercialized technology, having outstanding potential to open new opportunities in chemistry, sustainability, and beyond.

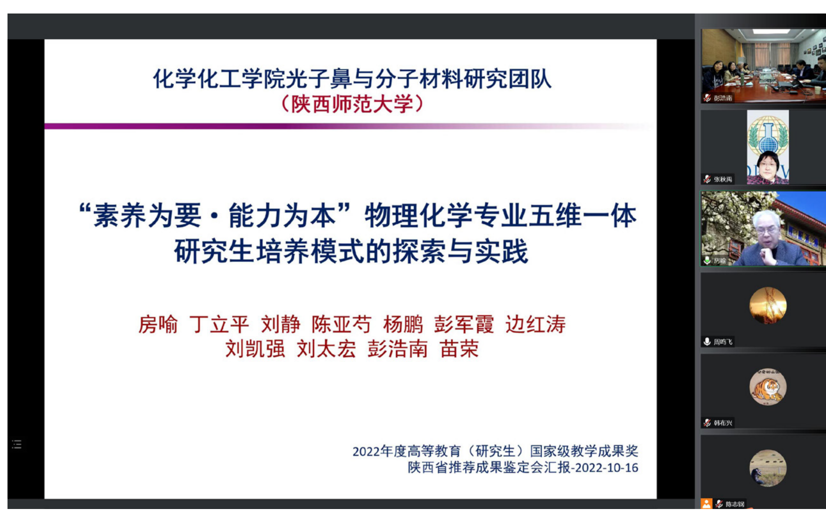
The International Union of Pure and Applied Chemistry (IUPAC) was founded in 1918 as the International Congress of Applied Chemistry, whose mission is to address issues related to the discipline of chemistry of global concern. Its widely recognized representative work is to unify the naming standards for chemical elements and their compounds, and has the final decision on element naming and symbolization.

IUPAC 发布网址：https://iupac.org/iupac-2022-top-ten/
Link of IUPAC release: https://iupac.org/iupac-2022-top-ten/
Chemistry International 文章链接：https://doi.org/10.1515/ci-2022-0402
Link of Chemistry International article: https://doi.org/10.1515/ci-2022-0402

团队研究生培养成果通过鉴定获推荐参评国家级奖

Fang Group's Postgraduate Cultivation Mode recommended for national award





10月16日上午，光子鼻与分子材料团队的《“素养为要·能力为本”物理化学专业五维一体研究生培养模式的探索与实践》教学成果通过省教育厅组织的鉴定，获推荐申报高等教育（研究生）国家级教学成果奖。

此次鉴定会由陕西省教育厅组织并在线召开，中国科学院化学研究所韩布兴院士担任鉴定组组长，西北大学王尧宇教授、北京大学黄建滨教授、复旦大学周鸣飞教授、西北工业大学张秋禹教授为组员。

团队负责人房喻院士、成员丁立平教授、刘静教授、刘凯强研究员、边红涛教授、彭军霞副教授、刘太宏副教授参加鉴定会并进行了汇报和答辩。

专家组听取了汇报，审阅了有关材料并进行了质询，经过评议形成鉴定意见，认为陕西师范大学化学化工学院房喻教授团队经过20年的实践探索，建立了基于“素养为要、能力为本”理念的五维一体物理化学专业研究型人才培养模式。依托该模式，培养了一批富有家国情怀，志向高远，能担重任的研究型人才。该成果出自研究生培养基层团队，理念先进，特色鲜明，成效突出，可借鉴、可复制，具有很好的示范作用和推广价值。

On October 16, the teaching achievement “Exploration and Practice of Literacy-focused and Capacity-based Five-dimensional Integrated Cultivation Mode for Physical Chemistry Graduate Student” developed by the Photonic Nose and Molecular Materials Group passed Shaanxi provincial appraisal and was recommended for national level teaching achievement award in higher education (postgraduate).

The online appraisal meeting was organized by the Shaanxi Provincial Department of Education, with CAS academician Prof. Han Buxing of the Institute of Chemistry of the Chinese Academy of Sciences as the head of the appraisal panel, Prof. Wang Yaoyu of Northwest University, Prof. Huang Jianbin of Peking University, Prof. Zhou Mingfei of Fudan University, and Prof. Zhang Qiuyu of Northwestern Polytechnical University as panel members.

Group leader Prof. Fang Yu, members Prof. Ding Liping, Prof. Liu Jing, researcher Liu Kaiqiang, Prof. Bian Hongtao, Assoc. Prof. Peng Junxia and Assoc. Prof. Liu Taihong attended the appraisal meeting and gave reports and defenses.

The panel listened to the report, reviewed the materials and put forth questions, and formed an appraisal opinion after deliberation. They believe that after 20 years of practice and exploration, the team of Prof. Fang Yu of the School of Chemistry and Chemical Engineering of Shaanxi Normal University has established a Literacy-focused and Capacity-based Five-dimensional Integrated Cultivation Mode for Physical Chemistry Graduate Student. Using this model, they have cultivated a group of research-oriented talents with patriotic feelings, lofty ambitions and ready to shoulder heavy responsibilities. The mode, coming from a grass-rooted postgraduate cultivation team, with advanced concept, distinctive characteristics, and outstanding results, can be learned and duplicated, and has a good demonstration role and promotion value.

简讯动态 News in Brief

最近，房喻教授受邀担任美国化学会主办的《物物理化学快报》（JPCL）顾问委员会委员。

Recently, Prof. Fang was invited to serve on the advisory board of The Journal of Physical Chemistry Letters (JPCL) sponsored by the American Chemical Society.

最近，房喻教授受邀担任“南方科技大学城市固体废弃物资源化技术与管理重点实验室（深圳市重点实验室）”学术委员会主任委员。

Recently, Prof. Fang Yu was invited to serve as the chairman of the academic committee of the Key Laboratory of Municipal Solid Waste Resource Technology and Management of Southern University of Science and Technology (Shenzhen Key Laboratory).

10 月 20 日，房喻教授应邀赴火箭军工程大学作报告。

On October 20, Prof. Fang Yu was invited to give a report at the Rocket Force Engineering University.

10 月 21 日，房喻教授应邀参加广东省高等学校聚集体科学基础研究卓越中心（线上）会议。

On October 21, Prof. Fang Yu was invited to attend the (online) meeting of Center for Excellence in Basic Scientific Research of Guangdong Province Universities Aggregate.

10 月 26 日，房喻教授线上参加中国化学会应用化学学科委员会全体委员大会。

On October 26, Prof. Fang Yu attended the online plenary meeting of the Applied Chemistry Committee of the Chinese Chemical Society.

ACS APPLIED MATERIALS & INTERFACES
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Research Article

Desolvation-Degree-Induced Structural Dynamics in a Rigid Cerium–Organic Framework Exhibiting Tandem Purification of Ethylene from Acetylene and Ethane

Han Fang, Bin Zheng, Zong-Hui Zhang, Peng-Bo Jin, Hong-Xin Li, Yan-Zhen Zheng, and Dong-Xu Xue*

去溶剂化程度诱导的一例刚性的动态铈基－有机骨架及其从乙炔和乙烷中串联纯化乙烯性能

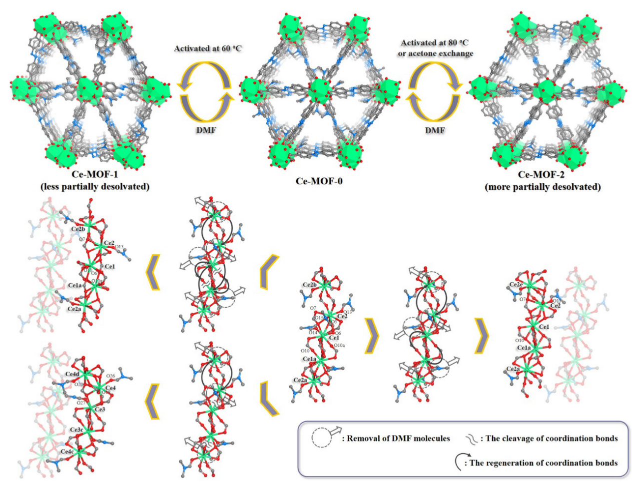

图 1. Ce–MOF–0 在不同条件下单晶到单晶的结构转变及其相应的棒状 MBB 的重排。Ce、C、O 和 N 分别用绿色、灰色、红色和蓝色的球体表示。为了清晰起见，省略了氢原子。

Figure 1. Single-crystal to single-crystal structural transformations of Ce-MOF-0 under different conditions and its corresponding rod-shaped MBB rearrangements. Ce, C, O, and N are represented by green, gray, red, and blue spheres, respectively. Hydrogen atoms are omitted for clarity.

乙烯是最重要的工业产品之一，其产量是衡量一个国家石化工业发展水平的一项重要标志。由于工业上对乙烯高产量和高质量的要求，从乙炔和乙烷中高效纯化乙烯是非常重要的，但也具有挑战性，而从乙炔和乙烷中吸附分离乙烯的工艺被认为是一种可行的节能技术。动态金属有机骨架 (MOF) 近年来展示了有趣的结构动力学和多种应用。其中，虽然一些柔性 MOF 表现出了有吸引力的乙烯净化能力，但刚性 MOF 在这方面的研究还鲜有报道。

基于此，我们通过溶剂热反应合成了一例具有结构动态的刚性铈基 MOF，即 Ce–MOF–0。该结构由连接有配位强度不同的 N,N– 二甲基甲酰胺的棒状分子构建单元与线性二羧酸酯桥连而成。由于中心金属离子的配位数灵活、羧酸酯的配位模式多变、以及弱配位的DMF分子的存在，通过不同温度加热或丙酮交换可发生不同的单晶到单晶结构转变，并成功得到了 Ce–MOF–1 和 Ce–MOF–2。两种新材料的去溶剂化程度略有不同，且中心金属配位几何和晶格参数略有变化，使得 Ce–MOF–1 和 Ce–MOF–2 分别表现出 C_2H_2 和 C_2H_6 的选择性吸附行为，即从 C_2H_2 和 C_2H_6 混合物中串联分离 C_2H_4 的潜在能力，这一结果也通过动态穿透实验得到了证实。

总的来说，这两种源于同一 MOF 的新材料能够串联实现从 C_2H_2/ C_2H_4/C_2H_6 的混合气中一步纯化 C_2H_4。这一工作为利用刚性

MOF 材料的动态结构实现先进的性能提供了新的思路。

第一作者：陕西师范大学硕士研究生方翰
通讯作者：陕西师范大学薛东旭副教授
全文链接：https://pubs.acs.org/doi/10.1021/acsami.2c13500

Ethylene is one of the most crucial industrial products and its production is one of the important signs to evaluate the development level of a nation's petrochemical industry. Due to the industrial requirements toward high production and high quality of ethylene, the efficient purification of ethylene from acetylene and ethane is of prime importance but challenging, and adsorptive separation processes of ethylene from acetylene and ethane are regarded as energy-efficient and practicable. Dynamic metal–organic frameworks (MOFs) have demonstrated intriguing structural dynamics and diverse applications recently. Among them, although a few flexible ones have exhibited interesting ethylene purification capability, rigid ones were yet barely investigated for such purpose.

Herein, a rigid cerium-based parent MOF of Ce-MOF-0 was originally isolated by means of solvothermal reaction, which displays structural dynamics and is built from rod molecular building blocks (MBBs) binding to distinct coordination strength of terminal N,N-Dimethylformamide (DMF) ligands, cross-linked by linear dicarboxylate linkers. Subsequently, two ultramicroporous daughter compounds of Ce-MOF-1 and Ce-MOF-2 were individually generated from Ce-MOF-0 upon distinguishing heat or acetone manipulations in a concerted fashion of single-crystal to single-crystal transformation. Due to the subtly distinct desolvation-degree of both new materials concomitant with slight variations of coordination geometry of central metal and crystal lattice parameters, Ce-MOF-1 and Ce-MOF-2 individually demonstrate C_2H_2- and C_2H_6-selective adsorption behaviour, resulting in potential tandem separations of C_2H_4 from C_2H_2 and C_2H_6 mixture. The results were also supported by dynamic breakthrough experiments.

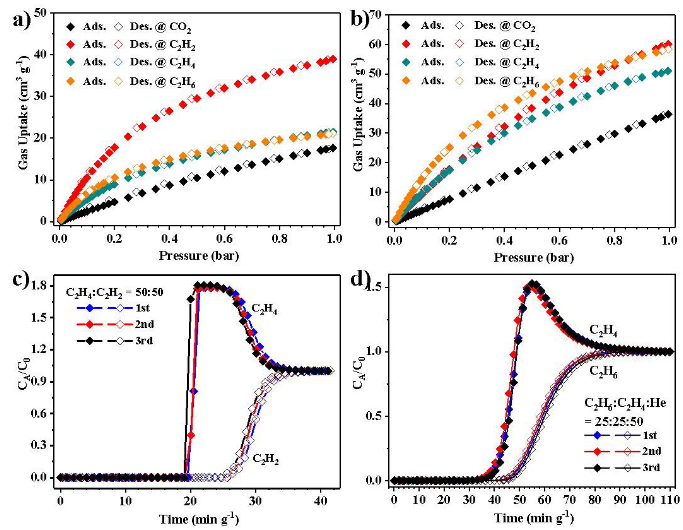

图 2. (a) 298 K 时 Ce−MOF−1 的 CO_2、C_2H_2、C_2H_4 和 C_2H_6 吸附和脱吸等温线。(b) 298 K 时 Ce−MOF−2 的 CO_2、C_2H_2、C_2H_4 和 C_2H_6 吸附和脱吸等温线；(c) Ce−MOF−1 在 C_2H_2/C_2H_4 (v/v, 50/50，2 mL min^{-1}) 流动条件下的穿透实验曲线和循环测试；d）Ce−MOF−2 在 C_2H_6/C_2H_4 (v/v, 25/25，6 mL min^{-1}) 流动条件下的穿透实验曲线和循环测试。

Figure 2. (a) CO_2, C_2H_2, C_2H_4 and C_2H_6 adsorption and desorption isotherms of Ce-MOF-1 at 298 K; (b) CO_2, C_2H_2, C_2H_4 and C_2H_6 adsorption and desorption isotherms of Ce-MOF-2 at 298 K; (c) Experimental column breakthrough curves as well as cycling tests for the C_2H_2/C_2H_4 (v/v, 50/50 under a flow of 2 mL min^{-1}) in an absorber bed packed with Ce-MOF-1; (d) Experimental column breakthrough curves as well as cycling tests for the C_2H_6/C_2H_4 (v/v, 25/25 under a flow of 6 mL min^{-1}) in an absorber bed packed with Ce-MOF-2.

In conclusion, both newly generated compounds derived from the same MOF would be capable of realizing tandem separations of C_2H_4 from C_2H_2 and C_2H_6. The present work may pave the way for rigid MOFs aiming advanced applications via solid-state structural dynamics.

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Full Text Link: https://pubs.acs.org/doi/10.1021/acsami.2c13500

ADVANCED MATERIALS INTERFACES

Research Article | Full Access

A Portable Fluorescence Sensor with Improved Performance for Aniline Monitoring

Xinxiang Gao, Rongrong Huang, Wan Fang, Wei Huang, Zihao Yin, Yue Liu, Xinyu Huang, Liping Ding, Haonan Peng, Yu Fang

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一种可用于苯胺监测的新型便携式荧光传感器

薄膜基荧光传感器的核心部件为荧光传感薄膜，其主要由薄膜基质和荧光单元两部分组成。其中荧光单元的种类、结构对薄膜传感性能发挥关键性作用，决定了传感单元和分析物之间相互作用的有效性。因此设计合成新型高性能荧光单元是研发薄膜基荧光传感器的基础。该课题组设计并合成了具有增强胺响应的邻碳硼烷改性均苯四甲二亚胺衍生物（CB–PMI）荧光材料，为肺癌的实时、可视化检测带来新的机遇。典型的 CB–PMI 分子由一个 PMI 核、两个苯环 (π – 桥) 和两个邻碳硼烷单元组成（图 1）。三维结构邻碳硼烷基团的引入赋予 CB–PMI 分子 AIE 特性。进一步，利用自制的传感平台评价了 CB–PMI 薄膜对苯胺气体的传感性能。它们对 1–50 ppt 浓度范围内的苯胺蒸气表现出灵敏、快速、选择性和线性的响应。

基于 CB–PMI 的荧光传感薄膜具有优越的胺响应性。苯胺作为一种有机胺，很容易被人体通过皮肤或呼吸吸收，具有很强的致癌性，并且苯胺被认为是肺癌的重要生物标志物。因此，使用实验室自制传感平台对基于 CB–PMI 的薄膜的传感性能进行评估。首先，将 CB–PMI 基传感膜暴露于 0.1 ppt 到 100 ppm 的不同浓度的气态苯胺后，其荧光强度随着苯胺浓度的增加而显着下降，且传感膜对含量从 1 到 50 ppt 的苯胺显示出良好的线性响应（图 2）。并且该传感体系的苯胺检出限可达 0.1 ppt，优于目前的已有报道。同时，与其他干扰分析物（100 ppm）相比较，传感膜对气态苯胺（10 ppm）表现出高选择性。

接下来探究了 CB–PMI 薄膜对苯胺蒸气传感的机理。研究发现 CB–PMI 的 HOMO 能级（–7.55 eV）低于苯胺的 HOMO 能级（–6.37 eV）。因此，当传感膜暴露于气态苯胺中时，苯胺分子将与 CB–PMI 相互作用，并将电子转移到 CB–PMI 的激发态，导

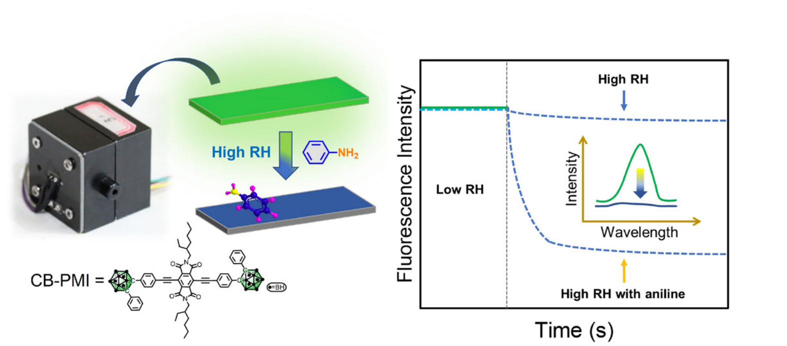

图 1. 在潮湿的环境中，基于 CB–PMI 所制薄膜荧光传感器的苯胺传感示意图。
Figure 1. Schematic illustration for the aniline sensing of CB-PMI-based fluorescence sensor under a humid atmosphere.

致光辐射过程的阻断。此外，敏感膜对苯胺蒸气的高灵敏度可能是由于荧光团的非平面结构，这种非平面结构可以诱导固态 CB–PMI 的松散堆积，促进苯胺在膜中的有效传质。为了验证这一假设，使用基于无碳硼烷化合物 Ph–PMI（具有平面分子结构）的传感膜对苯胺蒸汽进行了类似的灵敏度测试。虽然 Ph–PMI 的 HOMO 能量 (–7.11 eV) 也低于苯胺，但基于 Ph–PMI 的传感膜对苯胺和其他有机化合物的饱和蒸汽几乎没有响应。

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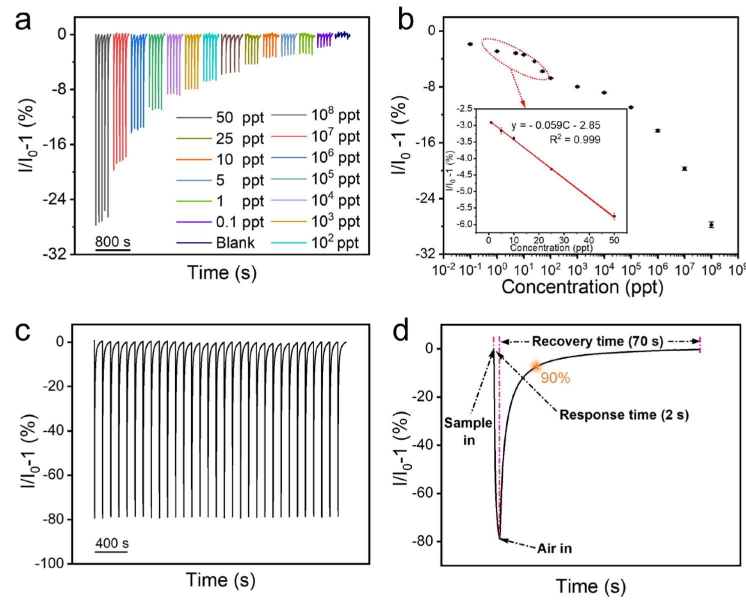

图 2. CB−PMI 传感膜的灵敏度和重复性测试
Figure 2. Sensitivity and repeatability test of CB-PMI sensing film

Fluorescent sensors have attracted much attention of scientists due to their outstanding advantages, such as high sensitivity, low cost, excellent selectivity, ease of sensor preparation, etc. In the sensing process, the first excited electronic state of a luminogen presents high sensibility to surrounding microenvironments including temperature, pressure, and solvent polority, thus the luminogens are of great significance. However, it is still challenging to design and synthesize novel luminogens that exhibit excellent photophysical characteristics, such as high luminescence, photostability, and high response specificity, for their applications in fluorescent sensors.

Herein, we designed and synthesized o-carborane modified pyromellitic diimide derivative (CB-PMI) fluorescent materials with enhanced amine-response, which offers the possibility for real-time and visual detection of lung cancer. The representative molecule CB-PMI consists of a PMI core, two phenyl rings (π-bridge), and two o-carborane units (Figure 1). The introduction of the o-carborane moieties with three-dimensional structure endows CB-PMI molecule with AIE characteristics. Subsequently, the sensing performance of CB-PMI films towards aniline vapor was evaluated with a homemade sensing platform, which showed a sensitive, rapid, selective, and linear response to aniline vapor in the wide range of 1 ppt to 50 ppt.

Fluorescence sensing film based on CB-PMI shows excellent amine response. Aniline as a kind of organic amine, can be easily absorbed by human beings through skin and/or via breathing, and is highly carcinogenic. Moreover, it is considered as an important biomarker for lung cancer. The sensing performance of thin films based on CB-PMI was evaluated on the self-made sensing platform in laboratory (Figure 2). Firstly, the fluorescence intensity of the CB-PMI-based film decreased significantly with the increase of aniline concentration after exposure to different concentrations of 0.1 ppm to 100 ppm of gaseous aniline. Obviously, the sensing film displayed a good linear response to aniline contents ranging from 1 ppt to 50 ppt. Moreover, this actual low detection limit (0.1 ppt) was much lower than that reported in previous studies for lung cancer detection.

Compared with other interfering analytes (100 ppm), the sensing film exhibited high selectivity to gaseous aniline (10 ppm).

We explored the sensing mechanism of aniline vapor based on CB-PMI thin film, and found that the HOMO energy (-7.55 eV) of CB-PMI was lower than that of aniline (-6.37 eV). Thereby, upon exposure of sensing films into gaseous aniline, the aniline molecules would interact with CB-PMI and transfer electrons to the excited state of CB-PMI, resulting in a blocking of the luminous radiation process. Moreover, the high sensitivity of the sensing film in responding aniline vapor could be resulted from the nonplanar structure of the fluorophore, which could induce loose packing of CB-PMI in the solid state, facilitating the effective mass transfer of aniline in the film. To verify the hypothesis, a similar sensitivity test for aniline vapor was conducted by using the sensing film based on the carborane-free compound Ph-PMI, which possesses a planar molecular structure. Although the HOMO energy (-7.11 eV) of Ph-PMI was also lower than that of aniline, the Ph-PMI-based sensing film presented almost no response to the saturated vapor of aniline and other organic compounds.

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A highly reusable fluorescent nanofilm sensor enables high-performance detection of ClO_2

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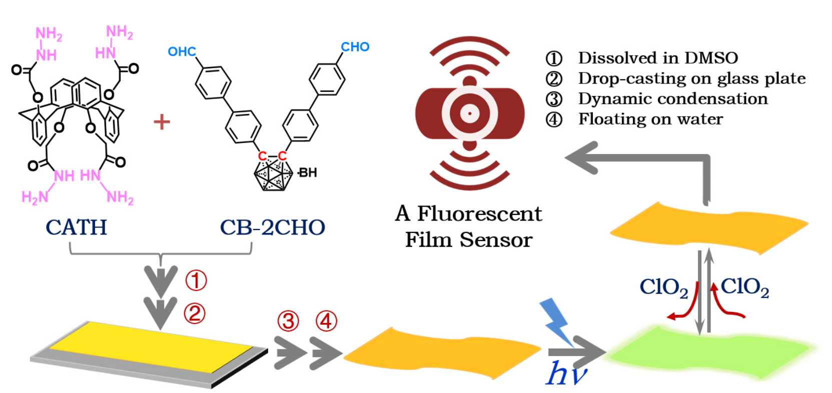
基于碳硼烷衍生物的荧光纳米薄膜的控制制备及其对二氧化氯的气相和液相检测

二氧化氯（ClO_2），作为第四代杀菌消毒剂，是国际上公认的一种无“三致效应”（致癌、致畸、致突变）的环保型杀菌消毒剂，在杀菌、食品保鲜、除臭、漂白等方面表现出非常显著的效果。因此，它被联合国世界卫生组织认定为一种安全、高效、强力的杀菌剂。然而，这些优势基于在适当的浓度下使用二氧化氯，而过量的二氧化氯会对人体呼吸系统和眼睛造成强烈的刺激。并且当空气中 ClO_2 体积浓度超过 10% 时，有爆炸危险。因此，不管是出于环境安全性的考虑，还是为保证二氧化氯的有效利用，可靠、简便的二氧化氯测定方法至关重要。

过去的几十年里，科研工作者陆续发展出诸如碘量法、紫外可见分光光度法、荧光法、电分析法等众多检测方法。尽管这些方法能够满足对二氧化氯检测浓度、成本、精度等方面的需求，



构筑单元 CATH 和 CB−2CHO 的分子结构，纳米薄膜的关键制备过程示意图以及基于纳米薄膜的二氧化氯荧光传感器。
Molecular structures of the two building blocks of CATH and CB-2CHO, and schematics of preparation of the nanofilms as well as the film-based fluorescent ClO_2 sensor.

但或多或少都存在一定的不足，最重要的是难以适用于现场实时在线原位检测。因此，研制出一种便携式传感器用于现场实时在线检测二氧化氯具有重大需求和重要意义。

基于此，我们设计和探索了一种新的荧光构筑基元，发展了一种新的荧光纳米薄膜，率先实现了对气相和液相二氧化氯的高性能荧光探测。本工作中，首先设计、合成了一种具有 AIE 性质的醛基功能化碳硼烷衍生物 CB–2CHO 和一种具有自组装性能的酰肼基功能化杯 [4] 芳烃衍生物 CATH。然后，采用以上两种砌块单元 CATH 和 CB–2CHO 在气液界面上通过动态共价缩合反应成功制备出了一种表面平整均匀、厚度及微观结构可控的高性能荧光纳米薄膜。此荧光纳米薄膜的厚度可实现从 80 nm 到 400 nm 的大范围精确调控。同时随着纳米薄膜厚度的增大，其微观结构依然能够保持多孔的三维网络状结构，这些无疑有助于提高荧光纳米薄膜的传感性能。基于该荧光纳米薄膜，在自主研发的传感平台上实现了对二氧化氯气体的高灵敏度、高选择性和快速可逆实时在线检测。其响应时间为 1 s，检出限可达 0.85 mg/L 且具有较宽的线性检测范围（0.85 mg/L ~ 5000 mg/L）。同时，常见物质对二氧化氯气体的检测几乎不产生干扰。因此，能够满足二氧化氯在低浓度以及高浓度时的实际检测需求。最后，利用薄膜基荧光传感器易于微型器件化的优势，概念性的构建了一种检测二氧化氯溶液的便携式传感器，利用该传感器实现了对泳池水中二氧化氯残留量的检测。我们相信该传感器在实现二氧化氯溶液的非接触式、快速可靠、实时在线，以及空气中二氧化氯的快速灵敏检测等方面将具有巨大的实际应用前景。

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Chlorine dioxide (ClO_2), as the fourth generation bactericidal disinfectant, is recognized to be an environmentally friendly disinfectant without “three causes” effects (carcinogenic, teratogenic, and mutagenic), and shows very significant effects in terms of sterilization, food preservation, deodorization, bleaching and other aspects. Therefore, it is identified as a safe, efficient, and powerful disinfectant by the World Health Organization. However, these advantages are based on the use of ClO_2 under proper concentrations as excessive ClO_2 can irritate the human respiratory system and eyes, and even cause acute kidney damage. There is also a risk of explosion when volume concentration of ClO_2 is more than 10 % in air. Thus, reliable, and facile method for ClO_2 determination is of great importance, which can not only guarantee the effective use of ClO_2 but also avoid the potential hazards.

Conventional detection methods for ClO_2 including chromatography, UV-Vis spectrophotometry, fluorescence techniques, electroanalysis have been developed for the convenient detection of ClO_2 over the past few decades. Although these methods can meet the requirements of concentration, cost and accuracy of ClO_2 detection, the most important problem is that they are difficult to be applied to on-site real-time in-situ detection. Therefore, it is of great importance to develop a portable sensor for on-site real-time and online detection of ClO_2. Based on this, we designed and explored a new fluorescence unit, developed a new fluorescence nanofilm, and achieved the first high performance fluorescence detection of ClO_2 in gas and liquid phases. In this work, CB-2CHO, an aldehyde functionalized carborane derivative with AIE properties, and CATH, an acylhydrazide functionalized calix[4]arene derivative with self-assembling properties, were designed and synthesized. Then, using CATH and CB-2CHO as building units at the gas-liquid interface through dynamic covalent condensation reaction, we successfully prepared a kind of high performance fluorescent nanofilm with uniform surface, controllable thickness and microstructure. The thickness of the nanofilm can be adjusted in a wide range from 80 nm to 400 nm, and the microstructures of the nanofilms can still maintain the porous three-dimensional network structures. All these will be beneficial to improve the sensing performance of fluorescent nanofilm. Based on the nanofilm, the high sensitivity, high selectivity and rapid reversible detection of ClO_2 vapor were realized on the homemade sensing platform. The response time for ClO2 was 1 s, the detection limit was ~0.85 mg/L, and it had a wide linear detection range (0.85 mg/L ~ 5000 mg/L). At the same time, common substances hardly interfered with the detection of ClO_2. Therefore, it can meet the actual detection demand of ClO_2 at low and high concentration. Based on this, we conceptually constructed a portable sensor, and then realized the detection of residual ClO_2 in swimming pool water. We believe that the sensor will have great practical application value in non-contact, fast and reliable, real-time on-line detection of ClO_2.

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狮子山下，我和我的同学们一起奋发向上的岁月

Under the Lion Rock, the days when my classmates and I strove for progress

文 / 马佳妮 by Ma Jiani

转眼间，新生入校已经两个月了，而我，博士毕业也快九年。往事历历在目，在此和同学们分享一些我的学习经历和感触。

2009 年夏天，我去香港大学读博士，在第一次与我的导师 David Lee Phillips 教授见面之前，我准备了大段的自我介绍和科研追求，希望给导师留下好印象。到了约定见面的时间，我敲开 David 的办公室，非常顺利地说完了我估计三四百字的“台词”，David 非常高兴，然后 blabla 地和我说了半个小时……然而，我一句也没有听懂。回到实验室，和各位师兄师姐说了我的经历，大家都笑了，并告诉我，老板是“美国乡村英语口音”，你只要告诉老板自己听不懂，老板就会放慢语速的。第二天，老板大清早来实验室和我们每个人聊了一会，并带着我看了一下课题组的激光器和光谱仪，然后说：“我们有这么多东西，你可以做科研了。”我高兴极了。

接下来的几天，每次老板来实验室总是会和几位师兄师姐，以及组里的博士后老师聊他们的

科研进展，而对我都是问候几句就结束了。我每每都想和老板讨论一下我的想法，但总是很紧张英语口音的问题，犹犹豫豫，不敢开口。直到一个周日的上午，老板居然来实验室了。因为根据学院的规定和老板的习惯，周日是休息日，所以实验室只有我一个人。他看见我在，露出很意外的神情，然后终于有机会我和他沟通了一上午的课题，自此敲定了我的想法，开始了实验。从此，我已经完全可以听懂他的英语口音。我想，如果那个周日我不在实验室，也许不能尽快地开始和导师沟通和交流。

想起当年，我给 David 发“套瓷”信的时候，他肯定不知道中国还有个西北大学。我工作后，没有仪器平台，每个寒假和暑假，都去老板课题组做实验。有几年，我没有博士名额，老板慷慨地让他的博士后协助我的工作。后来，我们发表了一些好的成果，我协助 David 申请到了陕西省百人计划的短期交流合作项目，他把拿到的奖励全部捐给了香港大学的科研经费。每每遇到困难，举步不前，David 总是给我安慰和鼓励。去年西安疫情封控期间，David 连发几封邮件问我是否一切都好。有一年，他来西安讲课交流结束后，我带他去兵马俑参观，一路上他和我讲了很多从事科研的感悟。我何其幸运能成为 David 的学生。

开始做实验了，这对我是很大的挑战。因为我硕士阶段的专业是高分子物理与化学，连打开激光器都不知道如何操作。老板请安慧颖师姐和李明德师兄指导我学习仪器使用。安师姐和李师兄是两种不同的风格，安师姐雷厉风行，李师兄细致包容。由于我态度认真，他们都很乐意教我。安师姐多次在组里对大家说：“小马是我唯一带过的师妹。”在他们的帮助下，我很快学会了仪器的操作。两个月后，我就拿到了所有的实验结果。

组里的官向国师兄看我很努力，笑言“孺子可教也”，就问我是否愿意学习用高斯做量化计算。于是，白天我就跟着师兄在电脑上敲各种类似代码的指令，晚上泡在小木虫论坛上学习量化计算的知识。因为计算是在 Linux 系统上进行，我还因此学习了很多关于 vi 的指令。组里当时还有位博士后 Dr. 马，常常会给我很多重要的指导。在师兄师姐们的无私帮助下，我终于可以独立开展课题了。我想，也是由于我谦虚好学的态度，打动了几位师兄师姐，才使得他们这些一路名校的人，对于天资并不聪慧的我，格外关照。

后来，老板拿到了一批经费，购置了超快瞬态吸收光谱平台。

培训的工程师走后，我们都还不懂如何操作。那个时候，明德师兄去了美国伯克利大学做博士后。我和同门同学苏涛商量后，决定真正把这套仪器学会并用起来。涛哥清华大学毕业，但是和我一样都没有光学和电子线路的基础。于是，我们采用了最简单的办法：每次改变一个光学器件的位置，就用记录下来对光谱质量的影响。这个过程花费了很多功夫，也真正学会了一些技术。好几次等我们调完光去楼下吃饭，才发现餐厅已经下班了。

按照组里的要求，都是学生自己要完成论文的写作，直到自己觉得达到能够发表的程度，才发给老板。我认真学习文献，特别是老板组里的文章，然后根据其中的逻辑和分析“照猫画虎”，硬是挤出了一篇文章。当时香港大学对非英语母语的学生开设了一门讲授英文科技论文写作的选修课，课上老师讲了很多非常实用的方法。比如，可以把看论文中自己认为的“好句子”摘录下来，或是给一个常用的词语，如 display，让我们去写近义词。这些训练极大、快速地提升了我的科技英语写作能力。我工作后指导研究生时，也告诉学生这样去学习。经过两轮修改后，我博士阶段的第一个工作顺利完成了，发表在 JOC 期刊上。

等到我博士第三年的时候，老板让我指导两位低年级的博士生。我们一起合作，互相促进，并发表了文章。在我们毕业多年后，还互相支持，官师兄虽然已经去了金融界，但是仍然在我遇到计算困境的时候，给我指导；明德师兄更是与我在科研上互相帮助，每每彼此遇到学术问题，还会互相讨论和交流；涛哥从中科院跳槽到了工业界，在我实验室搭建仪器的时候，还会周末飞来西安帮我调光；安师姐留在香港从事教育工作；我当年指导的师弟师妹，一个去了广州大学，一个从耶鲁大学完成博士后，进入香港科技大学工作。我想，同学之间的帮助、支持和学习，也是我们从事科研最宝贵的财富和收获。

我时常想念起，月明泉边，狮子山下，我和我的同学们一起奋发向上的岁月。

In the blink of an eye, it has been two months since the freshmen entered the university, and for me, I have graduated with a Ph.D. for almost nine years. I would like to share some of my learning experiences and feelings.

In the summer of 2009, I went to the University of Hong Kong for a PhD program. Before meeting my supervisor, Prof. David Lee Phillips, for the first time, I prepared a lengthy self-introduction and research pursuit, in the hope of making a good impression on him. When it was time of the appointment, I knocked on David's office door and finished the three or four hundred words of "lines" smoothly. David was very happy, and then blablared with me for half an hour ... However, I did not understand a word. When I returned to the laboratory and told other students about my experience, everyone laughed and told me that the boss has an "rural American English accent", and if you tell the boss that you don't understand, he will slow down. The next day, David came to the laboratory early in the morning. After chatting with us, he took me to see the laser device and spectrometer, and then said: "We have so many equipment. You can begin your research now." I couldn't be happier.

In the next few days, every time David came to the laboratory, he would always discuss their research progress with other students, as well as the postdoctoral researchers in the group, and say only a few words of greetings to me. I always wanted to discuss my ideas with him, but I was always nervous about the English accent and hesitated to speak. Until one Sunday morning, David showed up at the laboratory unexpectedly. Because according to the school rules and his habits, Sunday is a day off, so I am the only one in the laboratory. He saw me and looked surprised, and then I finally had the opportunity to communicate with him about my research topic for the whole morning, and soon I have finalized my idea and started experimenting. Since then, I can fully understand his English accent. I thought that if I wasn't in the lab that Sunday, I might not have been able to start communicating with my supervisor as soon as possible.

For several years, When I sent David the "Cotton-up" letter, he must not have known that there was a Northwest University in China. After I began to work in a university, I didn’t have a instrument platform, so I went to the David's laboratory to do experiments every winter and summer vacation. I didn't have any doctoral students, and David generously asked his postdoc to assist me. Later, after we published some good papers, I assisted David to apply for a short-term exchange and cooperation project of the Shaanxi Province Hundred Talents Program, and he donated all the fund he received to the research funds of the University of Hong Kong. Whenever I encountered difficulties and could not move forward, David always gave me comfort and encouragement. During the COVID lockdown in Xi'an last year, David sent me several emails asking if everything was okay. Once after he came to give a lecture in Xi'an, I took him to visit the Terracotta Warriors and Horses Museum, and along the way he told me a lot of insightful reflections on scientific research. How lucky I am to be David's student.

Experimenting was a big challenge for me. Because my master's major is Polymer Physics and Chemistry, I didn't even know how to turn on the laser device. David told Ms An Huiying and Mr. Li Mingde to instruct me to learn to operate the instrument. Having two different styles, Huiying is vigorous and resolute, and Mingde is meticulous and inclusive. Because of my serious attitude, they were happy to teach me. Huiying said to everyone in the group many times: "Jiani is the only fellow student I have ever instructed." With their help, I quickly learned how to operate the instrument. Two months later, I had all the results.

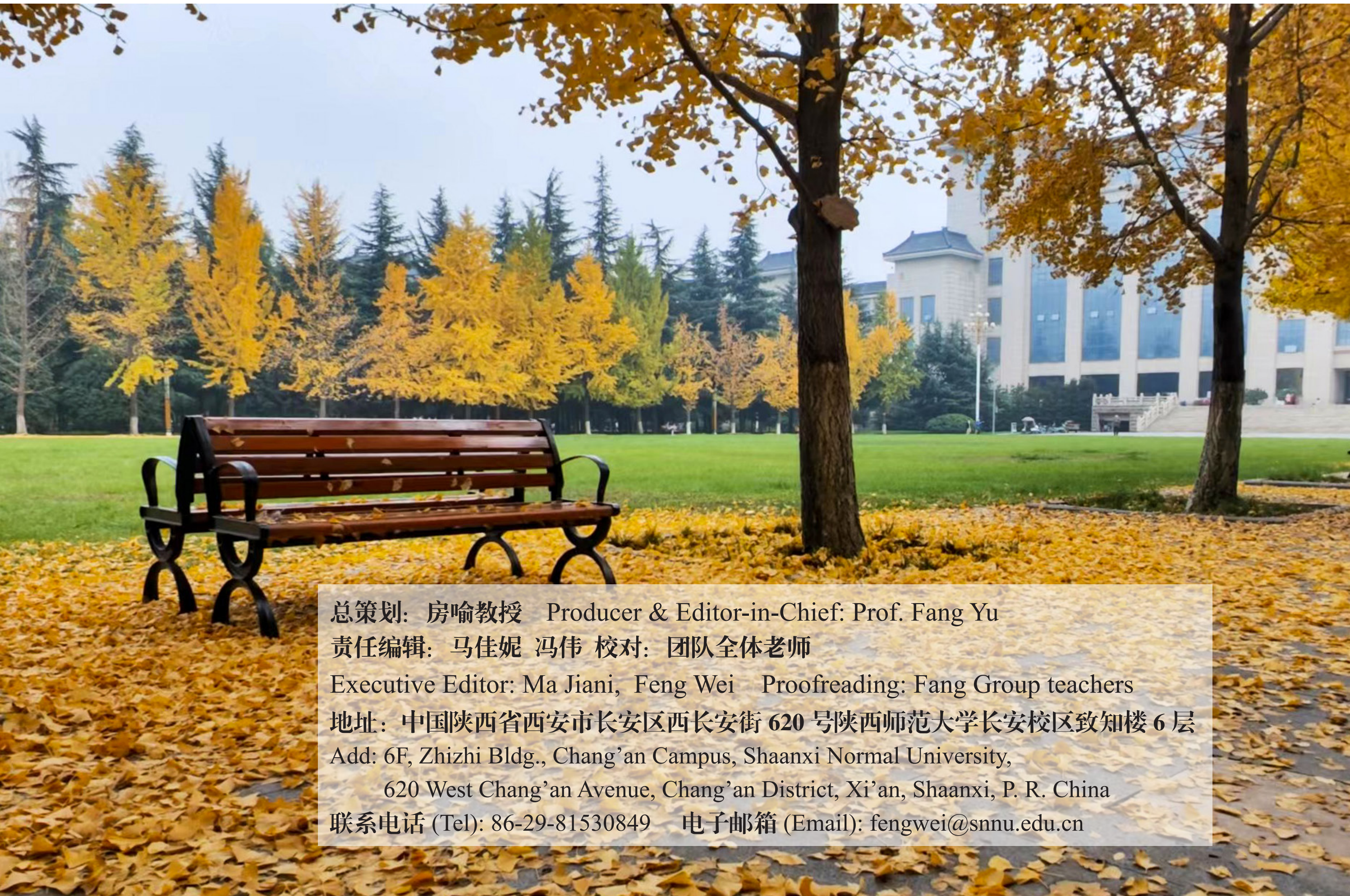
Mr. Guan Xiangguo of the group, seeing that I was working hard, said that "this student can be taught", so he asked me if I would like to learn to do Gaussian quantitative calculation. So, during the day, I followed Mr. Guan to type various code-like instructions on the computer, and at night I soaked in the Little Wood Worm forum to learn the knowledge of quantitative calculation. Since the calculations are done on Linux, I also learned a lot vi codes. There was also Dr. Ma, a postdoctoral fellow, there to help me at that time, giving me important advice and guidance. With the selfless help of my fellow students, I was finally able to carry out my research project independently. I think it is also because of my humble and studious attitude that impressed them, so that these people who have been studied in famous schools all the way were willing to help me, a person who is not talented.

Later, David got some fund and purchased an ultrafast transient absorption spectrometer. After the training engineers left, we still didn't know how to operate. By that time, Mingde had gone to the UC Berkeley in the United States as s postdoctoral fellow. After discussing with my classmate Su Tao, we decided to learn and use this instrument. Su Tao graduated from Tsinghua University, but like me, he had no knowledge or experience in optics and electronic circuits. So we used the simplest method: each time we adjust the position of an optic device, we record the effect on the spectral quality. It took a lot of effort, but we really learned some techniques. Several times when we finished the adjustment and went downstairs to eat, we found that the restaurant was already closed.

According to the rules of the group, students complete the writing of the thesis by themselves, and they do not send it to the supervisor until they feel it is publishable. I carefully studied the literature, especially the articles published by David’s group, and managed to finish an article according to the logic and analysis of these published articles, like "drawing the tiger with a cat as a model". At that time, the University of Hong Kong offered an elective course to teach English research paper writing for non-native English speakers, and the teacher taught many very practical methods in the class. For example, noting down what you think is a "good sentence" in a research paper, or writing synonyms of a commonly used word, such as display. The training greatly and quickly improved my academic English writing skills. When I begin to mentor graduate students, I also tell them to use this method. After two rounds of revision, the first work of my PhD stage was successfully completed and published in the journal JOC.

When I was in my third year of PhD program, David asked me to supervise two junior PhD students. We worked together, helped each other, and published articles. Many years after we graduated, we still support each other. Although Guan works in the finance, he still gave me guidance when I encountered computational difficulties. Mingde and I help each other in research, and whenever we encounter academic problems, we will discuss and communicate with each other. Su Tao left the Chinese Academy of Sciences to work in the industry, and he would fly to Xi'an on weekends to help me adjust light when I built instrument in my laboratory. Huiying stays in Hong Kong and works in education. One of the junior students I supervised went to Guangzhou University, and the other completed a postdoctoral program at Yale University and joined the Hong Kong University of Science and Technology. I think that the help, support and learning between fellow students are also the most valuable assets and gains for us to engage in scientific research.

I often think of the days, when my classmates and I worked hard and strove for progress, by the Chong Yuet Ming Fountain and under the Lion Rock.



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