陕西师范大学 SHAANXI NORMAL UNIVERSITY

化学化工学院 School of Chemistry & Chemical Engineering

新概念传感器与分子材料研究院 INSTITUTE OF NEW CONCEPT SENSORS AND MOLECULAR MATERIALS

新概念传感器与分子材料研究院 简报 02 2024

Institute of New Concept Sensors and Molecular Materials Newsletter

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陕西省副省长李钧看望慰问房喻院士

Shaanxi vice governor Li Jun visits Prof. Fang Yu

2024 年 2 月 4 日，陕西省副省长李钧到访新概念传感器与分子材料研究院，看望慰问房喻院士，送上节日的问候与祝福，并与房喻院士进行了座谈交流。李磊副校长陪同慰问。

On February 4, 2024, Shaanxi Province vice governor Li Jun visited Prof. Fang Yu at the Institute of New Concept Sensors and Molecular Materials, sending holiday greetings and best wishes, and they exchanged ideas in a discussion. Shaanxi Normal University vice president Li Lei accompanied the visit.

房喻院士出席陕西省 2024 年迎春团拜会

Fang Yu attends 2024 Spring Greeting Party of Shaanxi Province

2024 年 2 月 8 日，房喻院士出席在西安举行的陕西省 2024 年迎春团拜会。陕西省委书记、省人大常委会主任赵一德讲话，省长赵刚主持，省政协主席徐新荣出席。

现职省级领导同志，副省级以上老同志，省军区和武警陕西省总队负责同志，省直各部门、各人民团体、部分中央驻陕单位、香港特别行政区政府驻陕西联络处和新闻媒体主要负责同志，各界人士、外国驻陕人士代表约 350 人参加团拜会。

On February 8, 2024, Prof. Fang Yu attended the 2024 Spring Greeting Party of Shaanxi Province held in Xi'an.

Zhao Yide, secretary of the Shaanxi Provincial Party Committee and director of the Standing Committee of the Provincial People's Congress, delivered a speech at the event, which was presided over by Governor Zhao Gang, and Shaanxi Provincial CPPCC chairman Xu Xinrong also attended the meeting.

About 350 people, including current provincial leaders, veteran comrades at or above the deputy provincial level, heads of provincial military command and Shaanxi Armed Police Corps, provincial departments, people's organizations, some central units in Shaanxi, the Liaison office of the Hong Kong Special Administrative Region Government in Shaanxi and the news media, representatives from all walks of life and foreign representatives in Shaanxi attended the meeting.

房喻院士参加“催组装研究方法与理论基础”会议并作报告

Fang Yu presents at Conference of Research Methods and Theoretical Basis of Catassembly

2024 年 2 月 21 至 22 日，房喻院士应邀作为专家组组长及研讨会主持人参加了在厦门大学举办的“催组装研究方法与理论基础”基金委重大项目 2023 年度会议暨分子组装研讨会，并作题为《电子狗鼻 VS. CBRN 传感器——以薄膜荧光传感器为例》的学术报告。

此次会议由厦门大学化学化工学院和固体表面物理化学国家重点实验室共同主办。

From February 21 to 22, 2024, Prof. Fang Yu attended the 2023 Annual Conference of NSFC Major Project "Research Methods and Theoretical Basis of Catassembly" and Molecular Assembly Seminar held in Xiamen University as the expert group leader and seminar host, and presented a report titled "Electronic Dog Nose vs. CBRN sensors - A case study of film-based fluorescence sensors".

The conference was co-sponsored by the School of Chemistry and Chemical Engineering of Xiamen University and the State Key Laboratory of Physical Chemistry of Solid Surfaces.

房喻院士应邀出席智能传感交叉科学中心咨询会

Fang Yu attends consultation meeting of Smart Sensing InterScience Center

2024 年 2 月 27 日，房喻院士应邀赴天津出席由南开大学材料科学与工程学院主办的智能传感交叉科学中心咨询会。

On February 27, 2024, Prof. Fang Yu was invited to attend the consultation meeting of Smart Sensing Interdisciplinary Science Center hosted by the School of Materials Science and Engineering of Nankai University in Tianjin.

房喻院士出席国家毒品实验室陕西分中心第二届学术委员会会议

Fang Yu attends Second Academic Committee Meeting of National Anti-Drug Lab Shaanxi Center

2024 年 2 月 29 日上午，国家毒品实验室陕西分中心第二届学术委员会全体会议在陕西分中心会议室召开，学术委员会主任委员房喻院士主持会议，陕西省公安厅副厅长李向阳、陕西省公安厅禁毒总队政委王龙、全体学术委员会委员和陕西分中心全体民警参加了此次会议。

新概念传感器与分子材料研究院刘太宏副教授参与申报了一项陕西分中心开放课题，并作了题为《新精神活性物质高效检测的荧光技术开发和便携式设备研制》的学术进展报告。

On February 29, 2024, the Plenary Meeting of the Second Academic Committee of National Anti-Drug Laboratory Shaanxi Regional Center was held, and Prof. Fang Yu, Chairman of the Academic Committee, presided over the meeting.

Shaanxi Provincial Public Security Department deputy director Li Xiangyang, SPPSD Anti-Drug Corps political commissar Wang Long, members of the Academic Committee and all the police of the Shaanxi Branch participated in the meeting.

Associate Professor Liu Taihong of the Institute of New Concept Sensors and Molecular Materials submitted an open project application of Shaanxi Center, and presented a progress report titled “Development of fluorescence technology and portable equipment for efficient detection of new psychoactive substances”.

研究院教师获陕西省科技计划项目资助

INCSMM teachers funded by Shaanxi Science and Technology Projects

近日，陕西省科学技术厅公布了 2024 年度陕西省科技计划项目资助结果，新概念传感器与分子材料研究院 4 位教师获得资助。边红涛教授、刘静教授入选陕西省杰出青年科学基金资助计划，分别获资助经费 50 万元；刘小燕副教授获批陕西省自然科学基础研究重点项目，获资助经费 20 万元；薄鑫副教授获批陕西省自然科学基础研究青年项目，获资助经费 5 万元。

Recently, Shaanxi Provincial Science and Technology Department announced the results of the 2024 Shaanxi Science and Technology Program projects, and four teachers from the Institute of New Concept Sensors and Molecular Materials were funded.

Prof. Bian Hongtao and Prof. Liu Jing were funded by the Shaanxi Outstanding Youth Science Fund Program, receiving a funding of 500,000 yuan respectively; Assoc. Prof. Liu Xiaoyan was funded by a Key Project of Basic Research in Natural Science, receiving a funding of 200,000 yuan; and Assoc. Prof. Bo Xin was funded by a Youth Project of Basic Research in Natural Science, receiving a funding of 50,000 yuan.

ADVANCED SCIENCE
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Fully Reversible and Super-Fast Photo-Induced Morphological Transformation of Nanofilms for High-Performance UV Detection and Light-Driven Actuators

Xiangquan Liu, Jiahui Hu, Jinglun Yang, Lingya Peng, Jiaqi Tang, Xiaohui Wang, Rongrong Huang, Jianfei Liu, Kaiqiang Liu, Tingyi Wang, Xiaoyan Liu ✉, Liping Ding ✉, Yu Fang ✉

光诱导快速可逆形变纳米膜用于紫外检测和光驱动致动器

紫外线检测在军事和民用生活中都有广泛的应用。传统的紫外检测系统使用无机半导体材料，其柔韧性和可加工性较差。柔性光致变形材料已经被越来越多的用于软体机器人、人造肌肉和智能致动器的开发当中。本工作中，我们利用杯 [4] 吡咯 (CPTH) 四酰肼衍生物和三 (4– 甲酰苯基) 胺 (TFPA)，通过界面限域动态自组装的方法成功制备了柔性、自支撑、机械强度优异的纳米膜。通过利用纳米膜的光致变形特性，开发了一种全新的紫外探测系统，实现紫外光的实时在线探测 (图 1)。研究发现纳米膜在紫外光照下会发生变形，这种变形具有可逆性 (图 1)。所搭建的紫外探测系统检测范围为 2.85 μW cm^{-2} ~ 8.30 mW cm^{-2}，响应时间和恢复时间均小于 0.3 s，在 500 次连续测试中，紫外探测器具有较高的稳定性。复合膜超快的响应速度和超高灵敏度是由于在紫外光下纳米膜中大量酰腙键发生顺反异构。

此外，纳米膜还可以用于紫外光的可视化传感，纳米膜在不同的紫外线强度下可呈现不同的荧光图案。通过镀金处理将纳米膜作为智能开关实现了远程二极管 (LED) 发光控制。此外，将基于纳米膜的复合膜暴露在自然光下，花朵状的复合膜在不同紫外线强度下会呈现出多种姿态，设计的智能开关在太阳光的驱动下可以实现电动窗帘的自动控制 (图 2)。

此工作成功地制备了一种可逆的紫外响应纳米膜，构建了一种响应速度快、灵敏度高、可靠性强的紫外检测系统。此外，纳米复合膜可用做紫外线的可视化检测和实际场景中太阳光驱动智能开关及致动器，为光致变形材料实现快速、灵敏和稳定的紫外检测提供了新的机会。

第一作者：陕西师范大学博士研究生刘向泉
通讯作者：陕西师范大学房喻院士、丁立平教授、刘小燕副教授
全文链接：https://doi.org/10.1002/advs.202307165

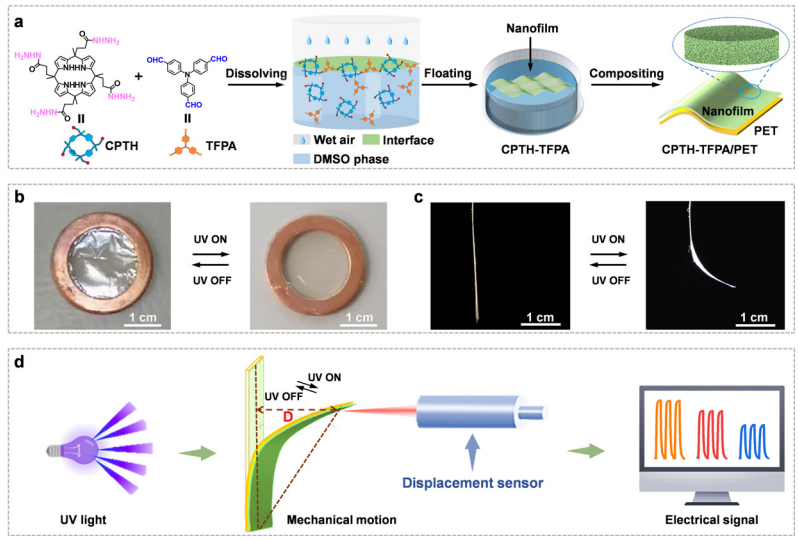

图 1. 纳米膜的制备及其光响应行为和紫外探测应用

Figure 1. Schematic representation of the preparation of an unique nanofilm and its application in UV detection.

UV light is widely utilized in both military and civilian applications. However, the rigid inorganic semiconductors and halide perovskites have limited flexibility and difficulties in machining, which make them be not suitable to develop flexible products. Recently, photo-deformable materials have garnered considerable attention across various areas, such as energy harvesting, soft robotics, artificial muscles, and switchable devices. Herein, a type of nanofilms with unprecedented fully reversible UV responsiveness are successfully constructed. Building upon this discovery, a new system for ultra-fast, sensitive, and reliable UV detection is developed. The system operates by monitoring the displacement of photoinduced macroscopic motions of the nanofilms based composite membranes. The system exhibits exceptional responsiveness to UV light at 375 nm, achieving remarkable response and recovery times of < 0.3 s. Furthermore, it boasts a wide detection range from 2.85 μW cm^{-2} to 8.30 mW cm^{-2}, along with robust durability. Qualitative UV sensing is accomplished by observing the shape changes of the composite membranes. Moreover, the composite membrane can serve as sunlight-responsive actuators for artificial flowers and smart switches in practical scenarios. The photo-induced motion is ascribed to the cis–trans isomerization of the acylhydrazone bonds, and the rapid and fully reversible shape transformation is supposed to be a synergistic result of the instability of the cis-isomers acylhydrazone bonds and the rebounding property of the networked nanofilms.

The composite membranes can also be used for visualized sensing of UV light. A fluorescent display system was constructed to show different fluorescent patterns under different UV intensity. Furthermore, a smart switch was created by coating a thin gold film on both sides of the composite membrane. When illuminated by UV light, the membrane bent downward, resulting in the activation of a light-emitting diode (LED) due to the completion of the electric circuit. Removal of UV light turned off the LED. The fabrication of a highly sensitive and super-fast UV-responsive artificial flower was designed to monitor UV light intensity at different times of the day. Another smart UV light-responsive switch was developed, enabling the automatic opening and closing of a curtain by controlling the motor's forward and reverse rotation.

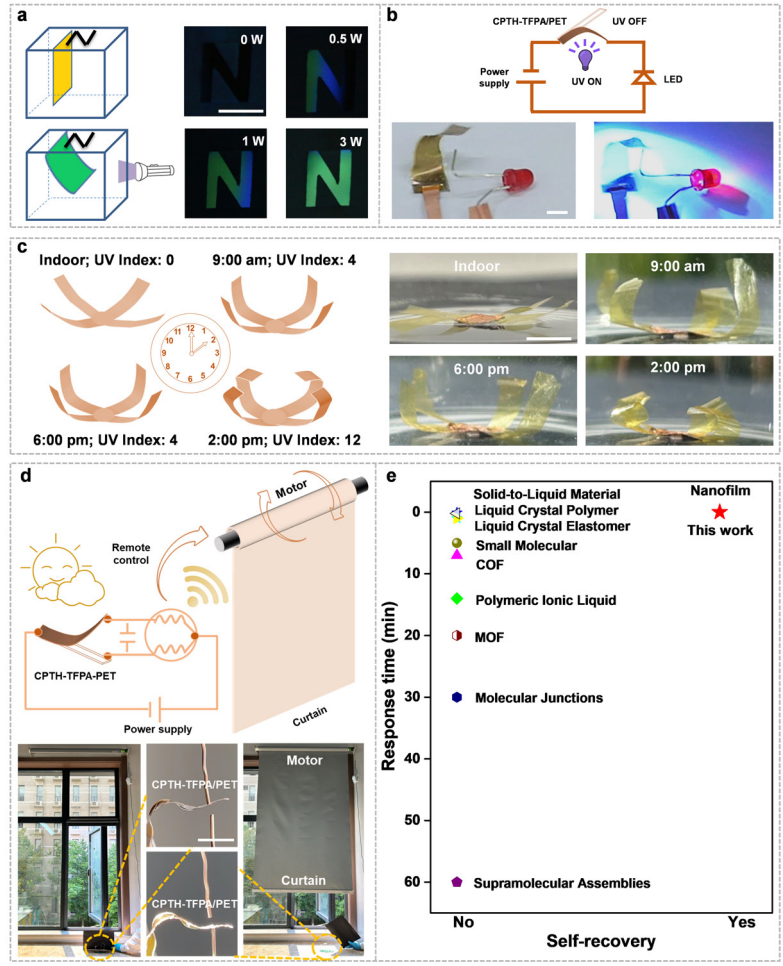

图 2. 纳米膜作为紫外光可视化传感器和智能开关在实际场景中的应用

Figure 2. The CPTH-TFPA/PET composite membrane act as a visual sensor of UV light and a smart switch in practical scenarios.

In summary, we have successfully created a high-performance UV detector based on the fast, robust, and fully reversible UV-responsive nanofilms. Importantly, the detection wavelength of the UV light can be largely adjusted by modifying the structure of the photo-responsive building block of the nanofilms. Furthermore, we have successfully achieved visual detection of UV light, enabling on-site, real time and power free sensing. Moreover, the composite membrane can serve as sunlight-responsive smart actuators for practical applications. The innovative CPTH-TFPA/PET membrane and our sensing model provide new opportunities for flexible organic materials to achieve fast, sensitive, and stable UV detection.

First Author: Liu Xiangquan, doctoral candidate, Shaanxi Normal University

Correspondence Authors: Prof. Fang Yu, Prof. Ding Liping, Assoc. Prof. Liu Xiaoyan, Shaanxi Normal University

Full Text Link: https://doi.org/10.1002/advs.202307165

analytical chemistry

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A Nanofilm-Based Fluorescent Sensor toward Highly Efficient Detection of Ethephon

Qianqian Liu, Rongrong Huang, Jiaqi Tang, Helan Zhang,* Mei Liu,* and Yu Fang*

基于纳米膜的高效检测乙烯利荧光传感器

植物生长调节剂（PGR）是广泛应用于农业和园艺的天然或人工物质，用于调节植物的生长发育。适当使用 PGR 可以帮助最大限度地提高作物产量、质量和对环境压力的抵抗力。乙烯利（ETH）是一种应用广泛的植物抗衰老活性物质，它通过释放乙烯在植物体内发挥作用，加速作物的成熟、脱落和衰老。然而，最大限度地发挥 ETH 的效益取决于适当的剂量和使用时间，因为不当使用可能导致作物毒性富集和过量残留，这对食品安全和环境健康构成重大威胁。事实上，ETH 的现场和实时可靠检测已经得到了广泛的关注。

目前，由于 ETH 分子量低、极性高、挥发性弱、缺乏颜色，现场和实时有效检测仍然是一个挑战。早期的气相色谱 (GC) 技术通过测定乙烯的释放量或甲基膦酸的产生量来间接定量 ETH。此外，还建立了液相色谱法、分光光度法、质谱法和电化学法。然而，这些方法不仅繁琐、耗时、功耗高、价格昂贵，所以排除了现场和实时使用的可能性。薄膜荧光传感器（FFSs）是一类新型的化学传感器，具有可设计性高、功耗低、体积小、操作方便、成本低、无污染等特点。此外，由于传感材料激发态特性固有的微环境敏感性，FFSs 通常具有高灵敏度和快速响应。事实上，在迅速侦测和识别隐藏的爆炸物、毒品、挥发性有机化合物以及其他有毒和危险化学品方面，FFSs 具有巨大潜力。

本研究开发了基于纳米膜的荧光膜传感器 (FFS)，实现了对气相中 ETH 的高效检测，检测限 (DL) 为 0.2 ppb，响应时间小于 10 s，且几乎不受干扰。传感器不同寻常的传感性能归因于纳米膜与 ETH 的特殊结合及其巨大的孔隙率，这使得有效的层传质成为可能。此外，还实现了基于可视化的定性感知。纳米膜是传感器的关键组成部分，在潮湿空气 /DMSO 界面上制备。所使用的构建块是特别设计的荧光邻碳硼烷衍生物 (CB–2CHO) 和具有三个酰肼基团的交联剂 BTN。制备的纳米膜具有柔韧性、均匀性、厚度可调、光化学超稳定性等特点。我们相信，我们的努力不仅解决了现场和实时检测 ETH 的挑战性问题，而且为通过传感膜创新开发新的 FFS 提供了另一条途径。

第一作者：陕西师范大学硕士研究生刘倩倩
通讯作者：陕西师范大学房喻院士、刘梅副教授、张荷兰高级工程师

全文链接：https://pubs.acs.org/doi/full/10.1021/acs.analchem.3c04999

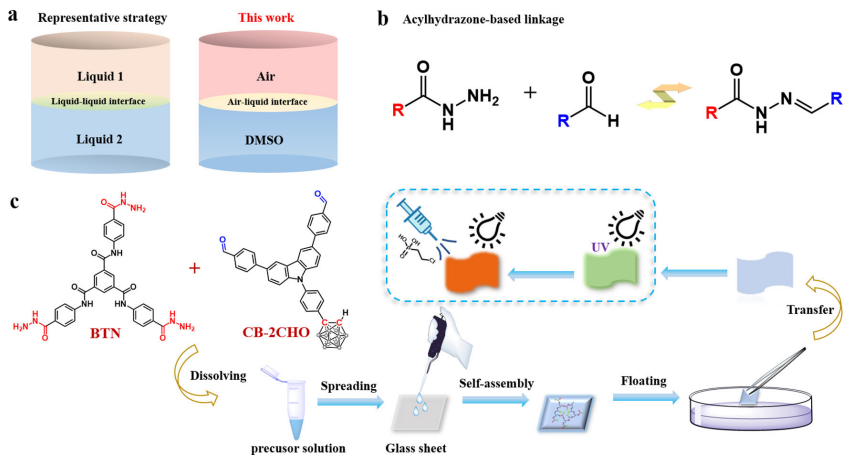

图 1. (a) 液 – 液界面和气 – 液界面纳米膜的合成；(b) 纳米膜形成过程中的动态共价反应；(c) 在潮湿空气 /DMSO 界面上制备纳米膜的基本结构和示意图。

Figure 1. (a) Synthesis of Nanofilms at Liquid-Liquid Interfaces and Air-Liquid Interfaces; (b) Dynamic Covalent Reactionduring Nanofilm Formation; (c) Structures of the Building Blocks and Schematic Representation of the Preparation of the Nanofilm at the Humid Air/DMSO Interface.

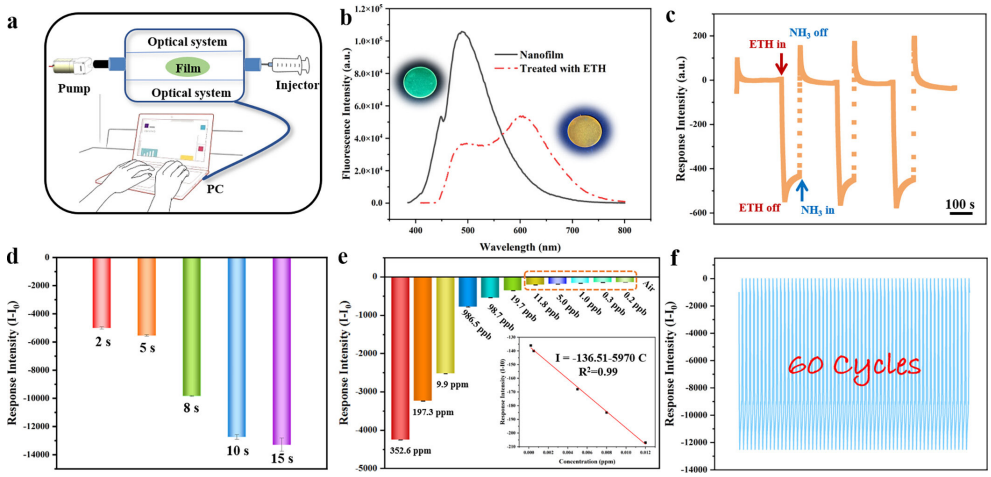

图 2. (a) 传感装置示意图，主要由供气装置、纳米膜传感器和数据采集系统三部分组成；(b) ETH 处理前后纳米膜的荧光发射光谱；(c) 反应轨迹的详细含义；(d) 采样时间优化；(e) 传感器对不同浓度 ETH 蒸气的响应，每次测量重复 5 次，插入的照片显示了响应强度与分析物蒸气浓度值之间的线性关系；(f) 基于纳米膜的传感器在 60 个周期连续测试后的再现性

Figure 2. (a) Schematic of the sensing device, which mainly consists of three parts, a gas supply unit, the nanofilm-based sensor, and a data collection system; (b) Fluorescence emission spectra of the nanofilm before and after ETH treatment; (c) Detailed meanings of the response traces; (d) Sampling time optimization; (e) Responses of the sensor to ETH vapor of different concentrations, where each measurement was repeated five times, and the inset photos show the linear relationship between the response intensity and value of the analyte vapor concentration; (f) Reproducibility for the nanofilm-based sensor upon 60 cycles continuous tests.

Plant growth regulators (PGRs) are natural or artificial substances that are widely used in agriculture and horticulture to regulate plant growth and development. Proper PGRs uses can help maximize crop yield, quality, and resistance to environmental stressors. Ethephon (ETH) is a widely used PGR and functions via releasing ethylene in plants to accelerate crop ripening, shedding, and senescence. However, maximizing the benefits of ETH depends on appropriate dosage and timing using as improper use could lead to crop toxicity enrichment and excessive residues, which poses significant threat to food safety and environmental health. In fact, on-site and at real-time reliable detection of ETH has gained widespread attention.

Currently, effective detection of ETH on-site and at real time still remains a challenge because of its low molecular weight, high polarity, weak volatility, and lack of colors. Early gas chromatography (GC) technique was developed to indirectly quantify ETH by determining the amount of ethylene released or methylphosphonic acid produced. Liquid chromatography, spectrophotometry, mass spectrometry, and electrochemical methods were also developed for the detection of ETH. These approaches, however, are not only cumbersome, time-consuming, high-power consumption and expensive, therefore ruling out the possibility for on-site and at real-time use. The film-based fluorescent sensors (FFSs) are a new class of chemical sensors, which possess the features of high designability, low power consumption, small size, easy operation, low cost, and even contamination free. Additionally, the FFSs generally exhibit high sensitivity and fast response due to the inherent microenvironment sensitivity of the excited state property of the sensing materials. In fact, the FFSs have been proven invaluable in rapidly detecting and identifying concealed explosives, drugs, volatile organic compounds, as well as other toxic and hazardous chemicals.

In this work, we developed a nanofilm-based fluorescence film sensor (FFS) and realized highly efficient detection of ETH in vapor phase, where the detection limit (DL) is <0.2 ppb, the response time is less than 10 s, and the interference is almost free. The unusual sensing performance of the sensor was ascribed to the specific binding of the nanofilm to ETH and to its great porosity, which enables efficient adlayer mass transfer, a requirement for high signal-to-noise ratio. Moreover, visualization-based qualitative sensing is also realized. The nanofilm, a key component of the sensor, was prepared at the humid air/DMSO interface. The building blocks used were a specially designed fluorescent o-carborane derivative (CB-2CHO) and a cross-linker BTN possessing three acylhydrazine groups. The nanofilm as prepared is flexible, uniform, thickness tunable, and photochemically super stable. We believe our effort not only addresses the challenging issue of on-site and at real-time detection of ETH but also provides another route for developing new FFSs via sensing film innovation.

First Author: Liu Qianqian, master's candidate, Shaanxi Normal University
Correspondence Authors: Prof. Fang Yu, Assoc. Prof. Liu Mei, Senior Engineer Zhang Helan, Shaanxi Normal University
Full Text Link: https://pubs.acs.org/doi/full/10.1021/acs.analchem.3c04999

analytical chemistry

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Interfacially Confined Dynamic Reaction Resulted to Fluorescent Nanofilms Depicting High-Performance Ammonia Sensing

Jingjing Liang, Dingfang Hu, Wenjun Xu, Lingya Peng,* Ke Liu,* and Yu Fang*

Cite This: *Anal. Chem.* 2024, 96, 2152−2157 Read Online

基于界面限域动态反应的荧光纳米薄膜用于高性能氨气传感

随着物联网、可穿戴设备、智能生活等相关产业的快速发展，传感技术和相关器件的发展意义日益凸显。在过去的二十年里，基于薄膜的荧光传感器（FFSs）领域的研究已经取得了令人瞩目的进步。然而，要满足实际应用中的需求，这些基于薄膜的荧光传感器必须达到一系列严格的标准，即所谓的“3S 1R”：灵敏度、安全性、速度和可逆性。除了这些基本要求外，良好的光化学稳定性也是评价荧光传感器性能的重要指标。因此，持续追求具有卓越性能的传感器具有紧迫意义。

利用特定的结构和性质，四配位硼分子被设计为荧光传感材料。已有研究对荧光四配位硼分子系统进行了研究，其具有极宽的温度可变范围，可以从 −80 到 60° C 实现温度监测。然而，所报道的基于硼配位荧光团的传感系统主要用于溶液状态下的传感，只有少数无溶剂系统被证明。因此，开发具有固态刺激响应特性的新型含硼材料变得重要。

在本工作中，我们引入了化学编织的概念，将硼配位的小分子固定在聚合物纳米薄膜中。通过设计一种含醛基的四配位硼荧光片段（NI−CHO）与一种酰肼片段 1,3,5− 均苯三酰肼（BTH）的界面限制动态反应，制备了四种荧光纳米膜。具有卓越的鲁棒性、且厚度在 40−1500 nm 范围内可调。其中薄膜 3 所制备的 FFSs 显示出对氨气（NH_3）的高度选择性和完全可逆的响应，检测极限小于 0.1 ppm，响应时间为 0.2 s。传感现象归因于荧光构

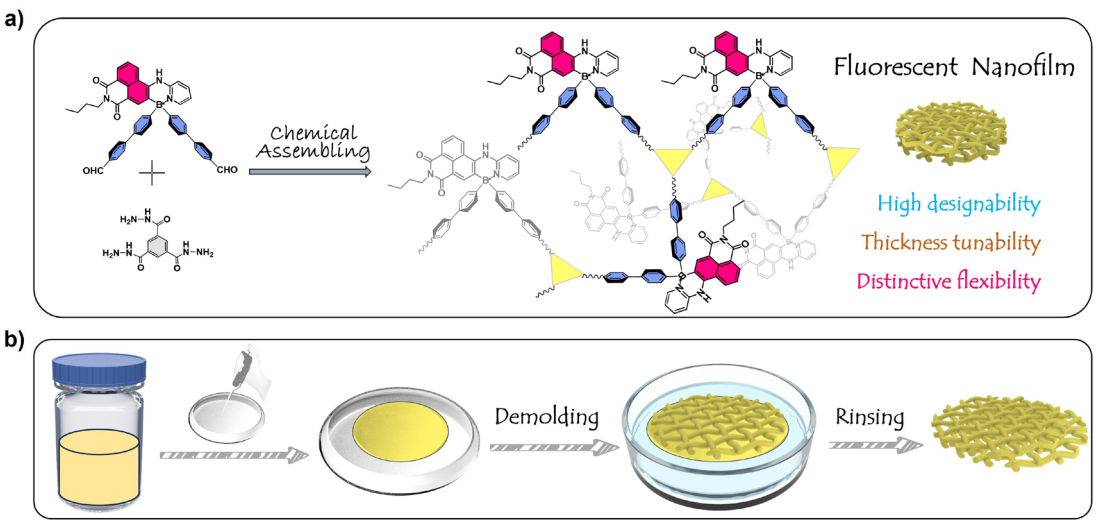

图 1. 纳米膜制备的示意图。

Figure 1. Schematics of the preparation of the nanofilm.

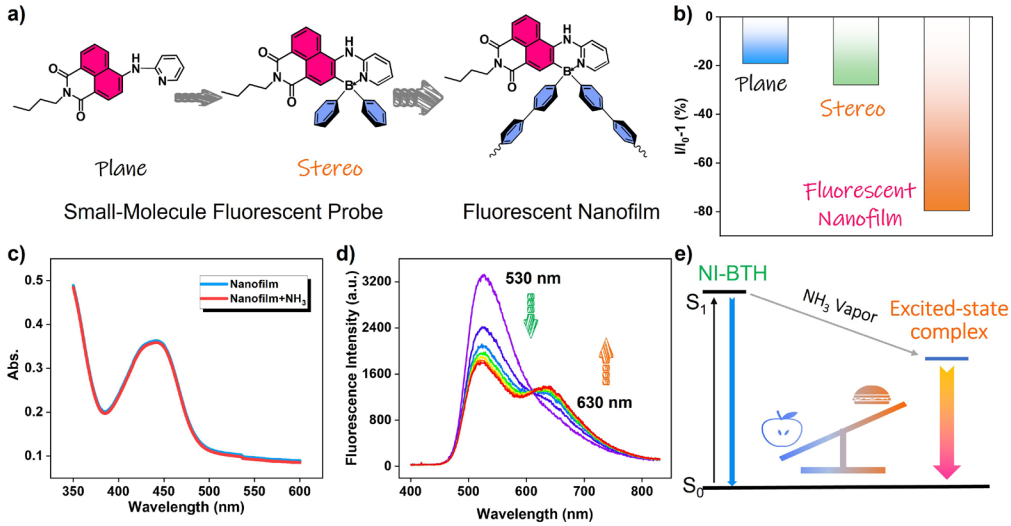

图 2. 便携式传感器对氨气的响应性能。

Figure 2. Response performance of portable sensors to ammonia.

建模块和分析物分子之间形成激发态荧光复合物，以及由于其多孔结构而导致的分析物分子的高效质量转移在分子层内的传输。我们相信，所提出的界面限域动态组装策略也可用于设计新的砌块，从而创造其他传感膜。

第一作者：陕西师范大学硕士生梁晶晶
通讯作者：陕西师范大学房喻院士、彭灵雅老师，西北农林科技大学刘科教授
全文链接：https://pubs.acs.org/doi/full/10.1021/acs.analchem.3c05032

With the rapid growth of industries related to the Internet of Things, wearable devices, and intelligent life, there has been an increasing recognition of the significance of development of sensing technologies and relevant devices. In the past twenty years, remarkable progress has been made in the field of film-based fluorescent sensors (FFSs). However, to meet the requirements of practical applications, these thin film-based fluorescence sensors must meet a series of stringent standards such as “3S + 1R” (sensitivity, selectivity, speed, and reversibility) and great photochemical stability. Therefore, the ongoing pursuit of sensing materials with superior performance is of urgent significance.

Using the specific structures and properties, boron-coordinated molecules were designed as fluorescence sensing materials. Research has been conducted on the fluorescent tetrahedral boron molecular system, which has an extremely wide temperature variable range and can achieve temperature monitoring from -80 to 60°C. Nevertheless, the sensing systems based on boron-coordinated fluorophores are predominantly utilized in solution state, with only a few instances of solvent-free systems being demonstrated. The inherent limitation in device making of the reported systems in solution state makes it important to develop new boron-containing molecular materials with solid-state stimulus-responsive properties.

In this context, we introduce the concept of chemical weaving to immobilize boron-coordinated small molecules into polymeric nanofilms. we fabricated four nanofilms via interfacially confined dynamic reaction of one specially designed fluorescent building block boron-coordinated molecular fragment (NI-CHO) with a known compound benzene-1,3,5-tricarbohydrazide (BTH) of multiple reactive sites. The nanofilms as prepared are fluorescent and show superior robust, flexible, uniform, thickness tunable, and self-adhesive properties. Especially, one of the four nanofilms, Film 3, depicted highly selective, sensitive, fast, and reversible sensing performance towards NH3 vapor. The experimental detection limit (DL) is lower than 0.1 ppm, and the response time is shorter than 0.2 s at room temperature. The reasons behind the sensing are ascribed to the formation of an excited-state fluorescent complex between the fluorescent building block and the analyte molecule as well as the efficient mass transfer of the analyte molecules within the adlayer owing to its porous structure. We believe that the presented interfacially confined dynamic assembly strategy can be also used for the creation of other sensing films through the innovative design of new building blocks, which function as sensing units.

First Author: Liang Jingjing, doctoral candidate, Shaanxi Normal University
Correspondence Authors: Prof. Fang Yu, Lecturer Peng Lingya, Shaanxi Normal University, and Prof. Liu Ke, Northwest A&F University
Full Text Link: https://pubs.acs.org/doi/full/10.1021/acs.analchem.3c05032

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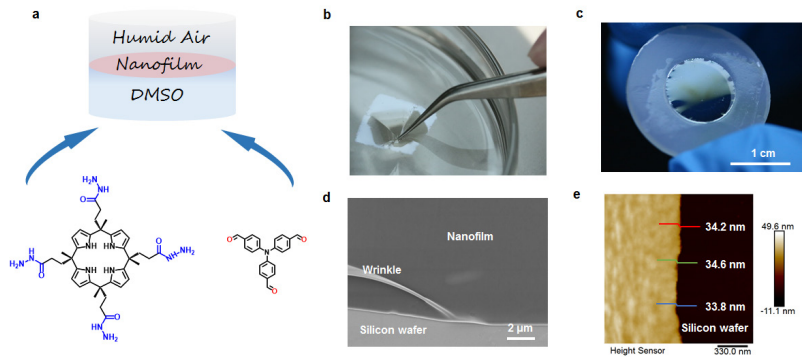
Efficient Removal of Iodine from Water by a Calix[4]pyrrole-Based Nanofilm

Tingyi Wang, Xiangquan Liu, Jinglun Yang, Jiaqi Tang, Binbin Zhai, Yan Luo, Zhongshan Liu,* and Yu Fang*

杯 [4] 吡咯基纳米膜对水中碘的高效去除

核能为技术进步和社会发展作出了巨大贡献。另一方面，它产生了大量的放射性废物，这对环境和公众健康构成了严重的威胁。铀裂变产生的放射性碘同位素 (^{131}I 或 ^{129}I) 是众多辐射源之一。放射性碘 (^{129}I) 毒性大，半衰期长 (1.57 × 107 年)，辐射强，迁移率大，需要被妥善处理。因此，如何从气相或溶液中捕获碘成为了急需考虑的问题。迄今为止，大多数研究都集中在从气相或者有机溶剂中捕获碘。从水溶液中吸附碘的研究相对较少但也同样重要。在现实环境中，受放射性碘污染的水主要有两个来源，即核电站 (如切尔诺贝利和福岛) 的废水排放和医院。此外，碘也是在紧急情况下使用的水消毒剂。尽管废水在排放前严格执行了防护程序，但残留的碘 (例如 5–32 mg/L) 仍然是有害的。因此，开发能够从水中去除微量碘的技术是非常必要的。

吸附法是工业上常用的去除 ^{129}I 的方法。已经报道的吸附剂主要有银基固体吸附剂、活性炭、金属交换沸石、粘土等。最近，一些具有高比表面积和可控多孔结构的新型吸附剂，如金属 – 有机框架 (MOFs)、共价有机框架、多孔芳香框架和其他多孔有机聚合物，已经被用于捕获碘蒸气。已经报道地用于从水溶液中捕获碘的吸附材料不仅有限，而且还存在一些缺点。例如，基于纳米材料的吸附剂容易聚集，这会降低结合位点的利用率。对于以多孔材料为主的吸附剂，由于结合位点常位于内部孔隙的表面，可用的结合位点比例受到限制。而膜分离技术因其去污系数高、占地面积小、能耗低等优点成为另一种从水溶液中捕获碘的方法。例如，聚合物 / MOFs 复合膜被用于快速去除水溶液中的碘。



然而，需要指出的是，大多数研究主要集中在高浓度碘的去除上，而同样具有重要性和挑战性的微量碘的去除似乎被忽视了。在本章的研究中，我们尝试采用纳滤的方式去除水相中的微量碘，以达到水的深度净化。因此，设计了一种无缺陷、自支撑的杯 [4] 吡咯基纳米膜，并将其用于碘污染水的深度净化。探讨了其吸附机理。

从水溶液中有效去除放射性碘在很大程度上取决于所采用的吸附材料。在这项工作中，我们报道了一种基于杯 [4] 吡咯的纳米膜用以去除水中的碘。该膜是通过四酰肼杯 [4] 吡咯与 1,3,5– 三 –(4– 甲酰基苯基) 醛，在空气 / 二甲基亚砜 (DMSO) 界面上的动态缩合而成的。获得的纳米膜的厚度约为 35 nm，可以实现快速的传质和高比例的碘的可用结合位点。纳米膜对碘的准二阶吸附动力学常数为 ~ 0.061 $g \cdot g^{-1} \cdot min^{-1}$，比大多数报道的吸附材料高出 3 个数量级，。通过纳滤测试表明，纳米膜的吸附量为 1.48 $g \cdot g^{-1}$，去除率高，可重复使用。机理研究表明，席夫碱、吡咯和芳香分子对碘的结合起关键作用。我们相信，这项工作不仅为从水中有效去除放射性碘提供了一种新策略，而且为设计有效的碘吸

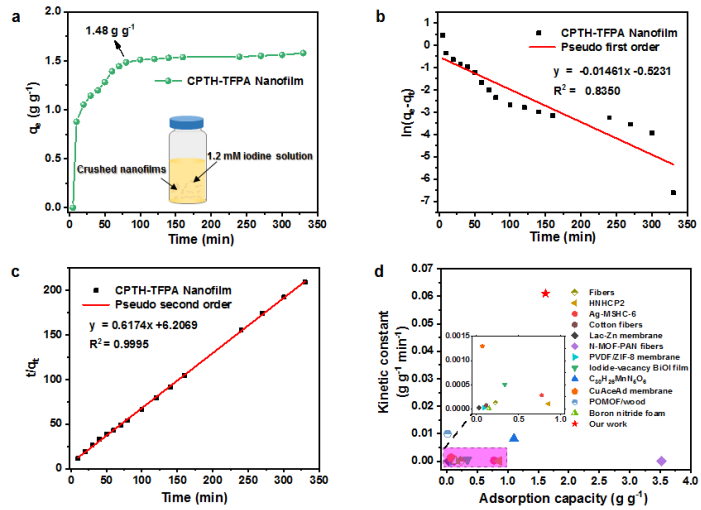
附剂提供了一些新的方法。

第一作者：陕西师范大学硕士研究生王挺屹
通讯作者：陕西师范大学房喻院士、刘忠山副教授

全文链接：https://doi.org/10.1021/acs.langmuir.3c03961

Nuclear energy has made great contributions to the progress of technology and the development of society. On the other hand, it produces massive radioactive wastes, which emerge as a serious challenge toward the environment and public health. Radioactive iodine isotopes (^{131}I or ^{129}I) generated by uranium fission are one of the numerous sources of radiation. The radioactive iodine (^{129}I) must be disposed properly as it features with high toxicity, long half-life (1.57 × 107 years), strong radiation, and large mobility. Therefore, capture of iodine from vapor phase or solution becomes a pre-requirement. To date, a great majority of studies have concentrated on the capture of iodine vapor or iodine from organic solvent. Relatively few but equally important studies have focused on iodine adsorption from aqueous solutions. Practically, water contaminated by radioactive iodine has been occurred by mainly two sources that are the discharge of wastewater from nuclear power plant (e.g., Chernobyl and Fukushima), and hospitals. In addition, iodine is also used as a water disinfectant, especially in emergencies. Although safeguard procedures are seriously implemented prior to discharge, the residual iodine (e.g.,5-32 mg·L-1) is still harmful. Thus, development of techniques for removal of trace iodine from water is highly needed.

Adsorption method is prevalent for industrial ^{129}I removal. The adsorbents reported include mainly silver-based solid adsorbents, activated carbons, metal-exchanged zeolite, clays, and others. Recently, new adsorbents with high surface areas and controllable porous structures, such as metal-organic frameworks (MOFs), covalent organic frameworks, porous aromatic frameworks, and other porous organic polymers, have been reported for iodine vapor capture.



The adsorbent materials usable for capture of iodine from aqueous solution are not only limited, but also suffer from some shortcomings. For example, the nanomaterials-based adsorbents are easy to aggregate, which will decrease the accessibility of the binding sites. For porous materials-based adsorbents, the ratio of accessible binding sites are limited due to their unfavorable locations, the surface of internal pores. Therefore, membrane separation technology has emerged as another method for the capture of iodine from aqueous solution because of their merits of high decontamination factor, large volume reduction and low energy consumption. For instance, polymer/MOFs nanocomposite membrane was used for the quick removal of iodine from aqueous solutions.

It is to be noted, however, that most studies are mainly focused on the removal of iodine at high concentrations, and the important and challenging removal of iodine at trace level seems to be ignored. In this work, we attempt to employ nanofiltration to removal trace iodine for deep purification of water. Accordingly, a defect-free, self-standing calix[4] pyrrole-based nanofilm was designed and used for the deep purification of iodine contaminated water. The adsorption mechanism behind was explored.

Efficient removal of radioactive iodine from aqueous solution is largely dependent on the adsorbent materials employed. In this work, we report a calix[4]pyrrole-based nanofilm and its application for the rapid removal of iodine from water. The nanofilm was synthesized through a confined dynamic condensation of tetra hydrazide calix[4]pyrrole with 1,3,5-tri-(4-formylphenyl) aldehyde at the air/dimethyl sulfoxide (DMSO) interface. The thickness of the obtained nanofilm is ~35 nm, enabling fast mass transfer and high ratio of accessible binding sites for iodine. The pseudo-second-order rate constant of the nanofilm for iodine is ~0.061 $g \cdot g^{-1} \cdot min^{-1}$, three orders of magnitude higher than most reported adsorbent materials. Flow-through nanofiltration tests demonstrated that the nanofilm has an adsorption capacity of 1.48 $g \cdot g^{-1}$, high removal efficiency, and good reusability. Mechanism study revealed that the moieties of Schiff base, pyrrole and aromatic rings play a key role for binding iodine. We believe this work provides not only a new strategy for efficient removal of radioactive iodine from water, but also new ideas for designing efficient iodine adsorbents.

First Author: Wang Tingyi, master's candidate, Shaanxi Normal University
Correspondence Authors: Prof. Fang Yu, Assoc. Prof. Liu Zhongshan, Shaanxi Normal University
Full Text Link: https://doi.org/10.1021/acs.langmuir.3c03961

THE JOURNAL OF PHYSICAL CHEMISTRY B
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Dynamics of Formamide–Water Mixtures Investigated by Linear and Nonlinear Infrared Spectroscopy

Yimin Bai, Jiman He, Yuting Gao, Miaomiao Zhang, Dexia Zhou, Yun Tang, Jing Liu, Hongtao Bian,* and Yu Fang

Cite This: https://doi.org/10.1021/acs.jpcb.3c07850 Read Online

甲酰胺 – 水混合溶液动力学的线性和非线性红外光谱研究

甲酰胺（FA）是一种含有酰胺键的分子，是能够形成 C=O・・・H 型和 NH・・・O 型氢键的最简单的分子之一。液态 FA 能够形成与水类似的三维氢键网络，这使得它们具有类似的性质，能够形成均匀的二元混合体系，为探索生物物理过程中肽键的溶剂化动力学提供了一个简化模型。本研究主要采用线性和飞秒红外光谱技术研究了 FA– 水混合物的动力学特性。通过研究 OD 局部探针和外源性探针 SCN^-，系统地探究了不同成分的 FA– 水二元混合物的氢键网络动力学行为。

在本研究中，OD 伸缩振动的弛豫动力学表明，添加 FA 对水分子振动寿命的影响可以忽略不计，这强调了该二元混合物类似于水的行为。然而，随着 FA 浓度的增加，OD 的转动动力学减慢，在 $X_{FA} > 0.5$ 后趋于稳定。这表明 OD 的转动时间与氢键网络的强度之间存在相关性，而这种变化很可能与溶液的介电常数变化相关。与此同时，SCN^- 的振动弛豫动力学与 FA 浓度有很强的相关性，表明在 SCN^- 溶剂化过程中水和 FA 分子之间存在竞争。此外，SCN^- 的转动时间常数与粘度变化呈线性关系，表明溶液的宏观粘度是由 FA 和水分子之间形成的扩展结构所决定的。本文还通过 Stokes–Einstein–Debye 方程分析了 SCN^- 的重定向动力学与宏观粘度之间的关系。观察到二元溶液的粘度 – 扩散耦合，这可以归因于 FA– 水混合溶

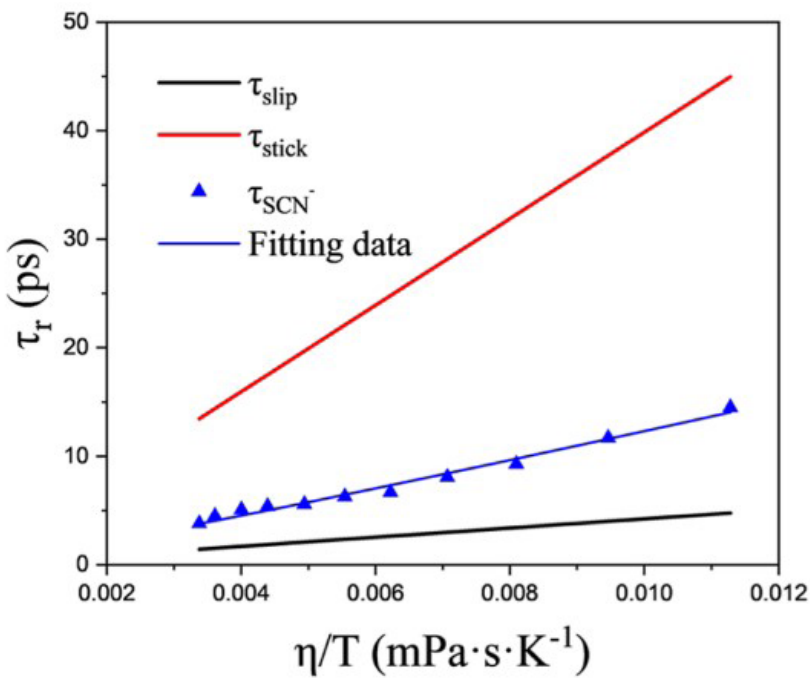


图 2. 不同浓度的 FA– 混合溶液中 SCN^- 的 τ_r 与 η/T 图及 Stokes–Einstein–Debye 理论预测两种情况下（粘着及滑移边界条件下）的曲线。蓝线表示拟合结果。

Figure 1. Plot of τ_r versus η/T for SCN– in different concentrations of FA–water mixture solutions and in the two cases of the hydrodynamic stick and slip boundary conditions represented by the red and black lines, respectively. The blue line represents the fitting result.

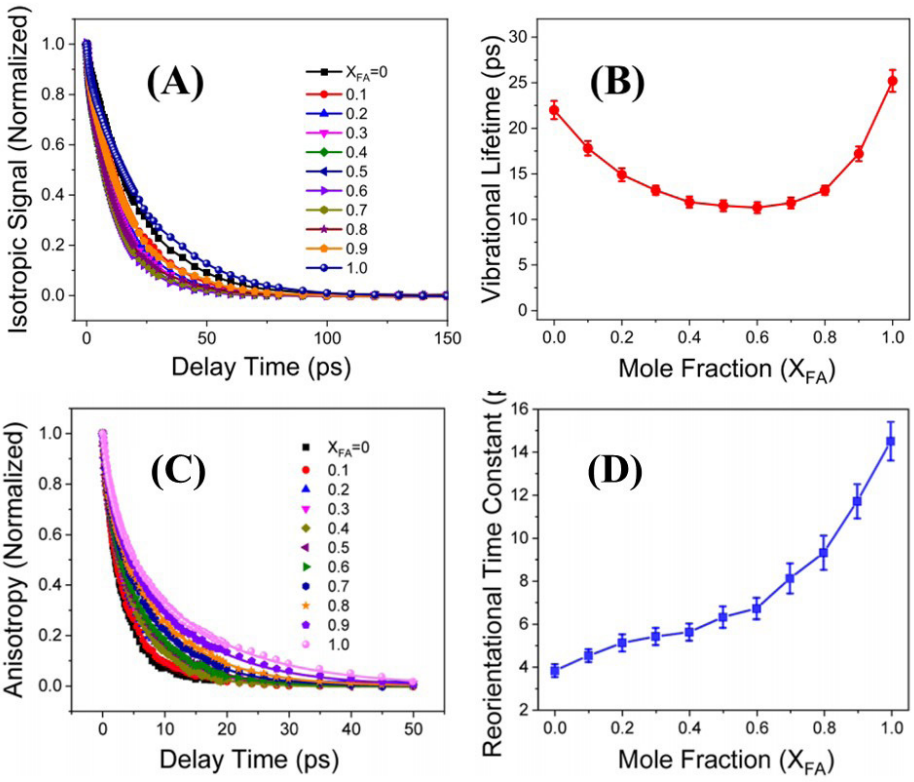


图 1. SCN^- 在浓度范围为 X_{FA}=0 ~1.0 的水溶液中 (A) 伸缩振动弛豫曲线；(B) 浓度依赖振动寿命；(C) 归一化各向异性衰减，实线为拟合数据；(D) 浓度依赖转动时间常数。

Figure 1. (A) Normalized vibrational population relaxation curves for the antisymmetric stretch of SCN^- in FA aqueous solutions with different concentrations. (B) Concentration-dependent vibrational lifetime (slow component) of SCN^- stretch (C) Anisotropy decay of SCN^- probe in the FA aqueous solutions. All the anisotropy decay curves are normalized to 1 at the delay time of zero. The solid lines are the fitting data using biexponential decay function. (D) Concentration-dependent rotational time constants of SCN^- stretch.

液的均匀动力学特性。这项研究阐明了 FA– 水混合物的氢键网络动力学，揭示了二元混合物溶液中的分子水平的均匀性的微观本质。

第一作者：陕西师范大学硕士研究生白亦敏
通讯作者：陕西师范大学边红涛教授
全文链接：https://doi.org/10.1021/acs.jpcb.3c07850

Formamide (FA) stands as one of the smallest molecules featuring amide bonds, enabling the formation of C=O···H and NH···O hydrogen bonds. The three-dimensional hydrogen bonds within liquid FA create a solvent-like state reminiscent of water's properties. Their mutual miscibility fosters microhomogeneous networks, rendering FA an invaluable model for studying essential biophysical processes driven by hydrogen bonding. This study is focused on the dynamics of FA−water mixtures using linear and femtosecond infrared spectroscopies. By using the intrinsic OD stretch and extrinsic probe SCN^-, the local vibrational behaviors and hydrogen bonding dynamics across various FA−water compositions were systematically investigated.

In this work, the vibrational relaxation of OD stretch revealed a negligible impact of FA addition on the vibrational lifetime of water molecules, underscoring the mixture's water-like behavior. However, the reorientational dynamics of OD stretch slowed with increasing FA mole fraction, plateauing beyond $X_{FA} > 0.5$. This suggests a correlation between OD's reorientational time and the strength of the hydrogen bond network, likely tied to the solution's changing dielectric constant. The vibrational relaxation dynamics of SCN− was strongly correlated with XFA, highlighting a competition between water and FA molecules in solvating SCN^-. There's also a linear relationship between rising viscosity and the prolonged correlation time of SCN^-'s slow dynamics indicates that the solution's macroscopic viscosity is dictated by the extended structures formed between FA and water molecules. The relation between the reorientation dynamics of the SCN^- and the macroscopic viscosity in aqueous FA−water mixture solutions was analyzed by using the Stokes−Einstein−Debye equations. The direct viscosity-diffusion coupling is observed, which can be attributed to the homogeneous dynamics feature in FA−water mixture solutions. This study offers fundamental insights into the dynamics of FA−water mixture solutions, highlighting their molecular-level understanding of the homogeneity within the binary mixture.

First Author: Bai Yimin, Master's candidate, Shaanxi Normal University
Correspondence Authors: Prof. Bian Hongtao, Shaanxi Normal University
Full Text Link: https://doi.org/10.1021/acs.jpcb.3c07850

西安市政府副秘书长看望慰问房喻院士

Deputy secretary general of Xi’an Government visits Prof. Fang Yu

2024 年 2 月 6 日，西安市人民政府副秘书长杨佐涛到访新概念传感器与分子材料研究院，看望慰问房喻院士，代表张涌副市长送上节日的问候与祝福。

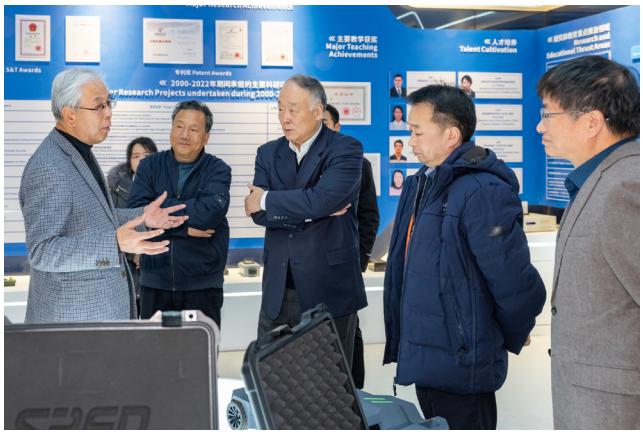
西安市委组织部公务员二处处长韩林儒等陪同慰问。

On February 4, 2024, Deputy secretary general of Xi’an Municipal Government Yang Zuotao visited Prof. Fang Yu at the Institute of New Concept Sensors and Molecular Materials, sending holiday greetings and best wishes on behalf of Xi’an vice mayor Zhang Yong.

Han Linru, director of the second Civil Servant Department of the Organization Department of the Xi’an Municipal Party Committee, accompanied the visit.

中国常驻联合国教科文组织原代表杨进来访

Former Representative of China to UNESCO Yang Jin received



2024 年 2 月 19 日，中国常驻联合国教科文组织原代表杨进到访新概念传感器与分子材料研究院，并与房喻院士进行了座谈交流。

陕西师范大学党委副书记卢胜利、陈鹏教授和李宗嗣老师陪同参加座谈交流。

On February 19, 2024, Yang Jin, former Permanent Representative of China to UNESCO, visited the Institute of New Concept Sensors and Molecular Materials and had a discussion and exchange with Prof. Fang Yu.

Shaanxi Normal University Party Committee deputy secretary Lu Shengli, Prof. Chen Peng and Mr. Li Zongsi accompanied the visit.

总策划：房喻教授
Producer & Editor-in-Chief: Prof. Fang Yu
责任编辑：丁立平 冯伟
Executive Editors: Ding Liping, Feng Wei
翻译：冯伟
Translator: Feng Wei
校对：团队全体老师
Proofreading: Fang Group teachers
地址：陕西省西安市长安区西长安街 620 号陕西师范大学长安校区
Chang’an Campus, Shaanxi Normal University, 620 West Chang’an Avenue, Chang’an District, Xi’an, Shaanxi, P. R. China
联系电话 (Tel)：86-29-81530726
电子邮箱 (Email)：incsmm@snnu.edu.cn
装帧设计：泛象艺术空间
Designed by FanForm Art Space