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Engineering the Interfacing of Molecules with 2D Transition Metal Dichalcogenides: Enhanced Multifunctional Electronics

*Bin Han, Paolo Samori**

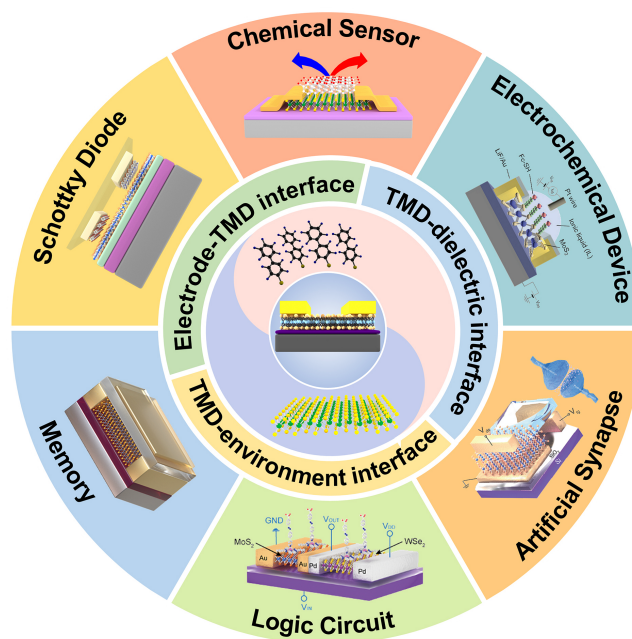
Université de Strasbourg, CNRS, ISIS UMR 7006, 8 allée Gaspard Monge, F-67000

Strasbourg, France.

CONSPECTUS

Engineering all interfaces between different components in electronic devices is key to control and optimize fundamental physical processes such as charge injection at metal-semiconductor interfaces, gate modulation at the dielectric-semiconductor interface, and carrier modulation at semiconductor-environment interfaces. The use of two-dimensional (2D) crystals as semiconductors, by virtue of their atomically flat dangling bond-free structure, can facilitate the tailoring of such interfaces effectively. In this context, 2D transition metal dichalcogenides (TMDs) have garnered tremendous attention over the past two decades owing to their

exclusive and outstanding physical and chemical characteristics, such as their strong light-matter interactions and high charge mobility. These properties position them as promising building blocks for next-generation semiconductor materials. The combination of their large specific surface area, unique electronic structure, and properties highly sensitive to environmental changes makes 2D TMDs appealing platforms for applications in optoelectronics and sensing. While a broad arsenal of TMDs has been made available which exhibit a variety of electronic properties, the latter are unfortunately hardly tunable. To overcome this problem, the controlled functionalization of TMDs with molecules and assemblies thereof represents a most powerful strategy to finely tune their surface characteristics for electronics. Such functionalization can be used not only to encapsulate the electronic material, therefore enhancing its stability in air, but also to impart dynamic, stimuli-responsive characteristics to TMDs and to selectively recognize the presence of a given analyte in the environment, demonstrating unprecedented application potential.



In this Account, we highlight the most enlightening recent progress made on the interface engineering in 2D TMDs based electronic devices via covalent and non-covalent functionalization with suitably designed molecules, underlining the remarkable synergies achieved. While the electrodes functionalization allows modulating charge injection and extraction, the functionalization of the dielectric substrate enables tuning of the carrier concentration in the device channel, and the functionalization of 2D TMDs upper surface allows to screen the interaction with the environment and imparts molecular functionality to the devices, making them versatile for various applications. The tailored interfaces enable enhanced device performance and open up avenues for its practical applications. This Account specifically focuses our recent endeavor on the unusual properties conferred to 2D TMDs through the functionalization of their interfaces with stimuli-responsive molecules or molecular assemblies. This includes, electrode-functionalized devices with modifiable

performance and charge carriers, molecular-bridged TMD network devices with overall enhanced electrical properties, sensor devices that are highly responsive to changes in the external environment, in particular, electrochemically switchable transistors that react to external electrochemical signals, optically switchable transistors that are sensitive to external light inputs, multi-responsive transistors that simultaneously respond to multiple external stimuli including optical, electrical, redox, thermal and magnetic inputs and their application in the development of unprecedented memories, artificial synapses, and logic inverters. By presenting the current challenges, opportunities, and prospects in this blooming research field, we will discuss the powerful integration of such strategies for the next-generation electronic digital devices and logic circuitries, outlining future directions and potential breakthroughs in interface engineering.

Key References

- Han, B.; Zhao, Y.; Ma, C.; Wang, C.; Tian, X.; Wang, Y.; Hu, W.; Samorì, P. Asymmetric Chemical Functionalization of Top-Contact Electrodes: Tuning the Charge Injection for High-Performance MoS₂ Field-Effect Transistors and Schottky Diodes. *Adv. Mater.* **2022**, *34*, 2109445.¹ *Molecular functionalization of electrodes in top-contact field-effect transistor was achieved. Asymmetric functionalization of the S/D electrodes enables Schottky diode with a rectification ratio of 10⁸.*

- Stoeckel, M.-A.; Gobbi, M.; Leydecker, T.; Wang, Y.; Eredia, M.; Bonacchi, S.; Verucchi, R.; Timpel, M.; Nardi, M. V.; Orgiu, E.; Samorì, P. Boosting and Balancing Electron and Hole Mobility in Single- and Bilayer WSe₂ Devices via Tailored Molecular Functionalization. *ACS Nano* **2019**, *13*, 11613-11622.² *Deterministic control and performance optimization of charge transport in 2D WSe₂ were achieved using molecular functionalization. The polarity can be adjusted from pure N-type to nearly balanced ambipolar to pure P-type.*
- Ippolito, S.; Kelly, A. G.; Furlan de Oliveira, R.; Stoeckel, M.-A.; Iglesias, D.; Roy, A.; Downing, C.; Bian, Z.; Lombardi, L.; Samad, Y. A.; Nicolosi, V.; Ferrari, A. C.; Coleman, J. N.; Samorì, P. Covalently Interconnected Transition Metal Dichalcogenide Networks via Defect Engineering for High-Performance Electronic Devices. *Nat. Nanotechnol.* **2021**, *16*, 592–598.³ *Dithiolated conjugated molecules are used to repair sulfur vacancies in liquid-phase exfoliated MoS₂ flakes and covalently bridge adjacent flakes to promote charge transport. Reproducible increase of an order of magnitude was achieved in mobility, current ratio, and switching time.*
- Qiu, H.; Herder, M.; Hecht, S.; Samorì, P. Ternary-Responsive Field-Effect Transistors and Multilevel Memories Based on Asymmetrically Functionalized Janus Few-Layer WSe₂. *Adv. Funct. Mater.* **2021**, *31*, 2102721.⁴ *Asymmetric functionalization of both sides of WSe₂ using ferroelectric molecules and photoresponsive molecules respectively realizes a multi-level memory with electric field and optical dual control. The device exhibits 756 distinct resistance states and a retention time of over 1000 hours.*

1 Introduction

Since the seminal experiment in 2004 by Geim and Novoselov⁵, demonstrating the outstanding physical properties of mechanically exfoliated graphene, there has been an ever-increasing interest in inorganic two-dimensional (2D) materials, especially in view of their electronic characteristics⁶⁻⁸. Despite graphene's high intrinsic charge carrier mobility, the lack of a bandgap has limited its potential for application in optoelectronics. As a result, other inorganic 2D materials, primarily layered transition metal dichalcogenides (TMDs), have gained increasing attention. These materials boast a tunable bandgap - from indirect bandgap conductors in bulk to direct bandgap semiconductors at the monolayer level - along with atomically thin structures, ultra-flat surfaces free of dangling bonds, outstanding optical properties, and high stability^{9,10}. Such attributes render TMDs versatile building blocks for applications in field-effect transistors (FETs), photodetectors, sensors, electroluminescent devices, integrated circuits, and wearable flexible devices^{11,12}. Consequently, TMDs have emerged as the most sought-after 2D semiconductor materials.

Owing to their distinctive 2D characteristics, TMDs exhibit a remarkably high sensitivity to environmental changes, which can result in the modification of their optical and electrical properties. Consequently, molecular functionalization of TMD electronic devices has emerged as a promising strategy to tailor their properties. Although molecular interface engineering has

been extensively explored in organic electronic devices over the last three decades, its application in ultrathin inorganic TMD electronic devices remains underexplored¹³⁻¹⁶. TMDs are phase-dependent materials, and in this manuscript, TMDs refer to the 2H semiconductor phase unless stated otherwise. Figure 1a-d display four planar FET device configurations utilizing TMD as the active semiconducting layer, categorized by the electrodes position: bottom-gate top-contact (BGTC), bottom-gate bottom-contact (BGBC), top-gate top-contact (TGTC), and top-gate bottom-contact (TGBC). These devices feature three critical interfaces that determine their electrical performance: the source/drain electrode-semiconductor interface, the semiconductor-dielectric interface, and the semiconductor-environment interface. Each of these interfaces can be individually or simultaneously functionalized using molecules, including asymmetric modifications to the source and drain electrodes, being crucial for optimizing device performance. Figure 1e depicts a TMD-based FET device with all three interfaces being molecularly functionalized. Molecular functionalization, involving both physical and chemical adsorption, can effectively modify interface properties, thereby modulating device performance¹⁷.

This Account is dedicated to engineering interfaces in TMD-based FETs using molecules and assemblies thereof as a route to optimize electrical properties and render the devices multifunctional.

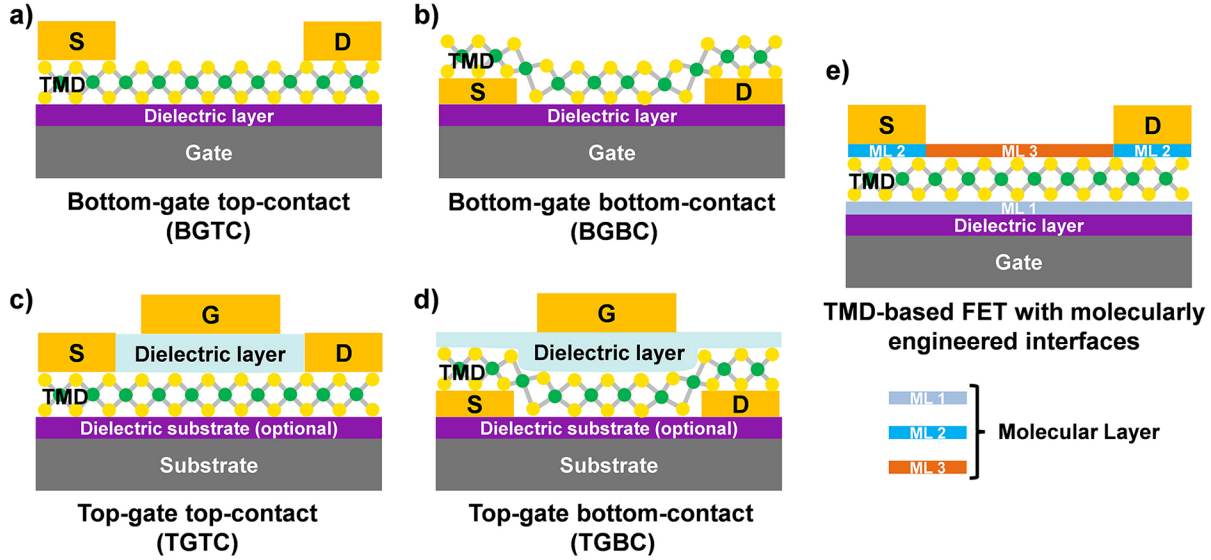


Figure 1. Scheme of TMD-based FET device configurations: (a) BGTC. (b) BGBC. (c) TGTC. (d) TGBC. (e) TMD-based FET with molecularly engineered interfaces.

2 Molecular Engineering of Electrode-TMD Semiconductor Interface

In any electronic device, the optimization of the interface between the electrode and semiconductor is crucial for reaching high-performance. The electrical contact resistance represents a major bottleneck in transistors and it is caused by the energy level mismatch between the electrode and the semiconductor's Conduction Band (CB) or Valance Band (VB). This mismatch forms an injection barrier, significantly affecting the FET performance¹⁸. Adjusting the Schottky barrier height (SBH) at this interface is of paramount importance. This goal can be achieved by changing the metal electrode type, but such a strategy is limited by the availability of suitable electrode materials and compatibility with fabrication processes. Thus, electrode engineering by using molecular assemblies like self-assembled monolayers

(SAMs) represents a promising approach^{19,20}. These SAMs provide molecular-scale control over interface properties such as work function (WF), surface roughness, and hydrophobicity-hydrophilicity, among other properties, enhancing charge injection and device performance^{13,21,22}. Thiol molecules, with their sulfhydryl groups, bond covalently with metal surfaces like gold and silver, adjusting the electrode's WF through molecular orientation and dipole moment size. This fine-tuning aligns with the semiconductor energy levels, optimizing electrode functionality to minimize electrical contact resistance^{23,24}.

2.1 Molecular Functionalization of Bottom-Contact Electrodes

For bottom-contact electrodes in FETs, the chemisorption of SAMs is commonly used. While in organic FETs (OFETs), SAMs can influence the film quality of organic semiconductors, in TMDs-based FETs, they only affect the carrier injection and concentration^{15,25}. Matković et al.²⁶ investigated the use of pyrimidine-containing SAMs for interfacial band engineering at the interface between MoS₂ and Au electrodes to achieve contact-resistance-free bottom-contact FETs. The authors proposed that the pyrimidine-containing SAMs can modify the electronic structure of the interface, resulting in the modulation of electrode WF through molecular dipoles, yielding a reduction of the contact resistance exceeding two orders of magnitude when a suitable SAM is employed (Figure 2a). Li et al.²⁷ reported the characteristics of mono and bilayer MoS₂ on electrodes functionalized with photo-switchable azobenzene molecules. When MoS₂ is in contact with electropositive azobenzene molecules in the *trans* configuration, the PL spectrum shows n-doped features, whereas when the

photoisomerization is *cis*, the doping effect decreases, PL magnitude increases by a factor of 3.²⁸ This reveals the potential of photoisomerization of molecules functionalized electrodes for applications in FETs.

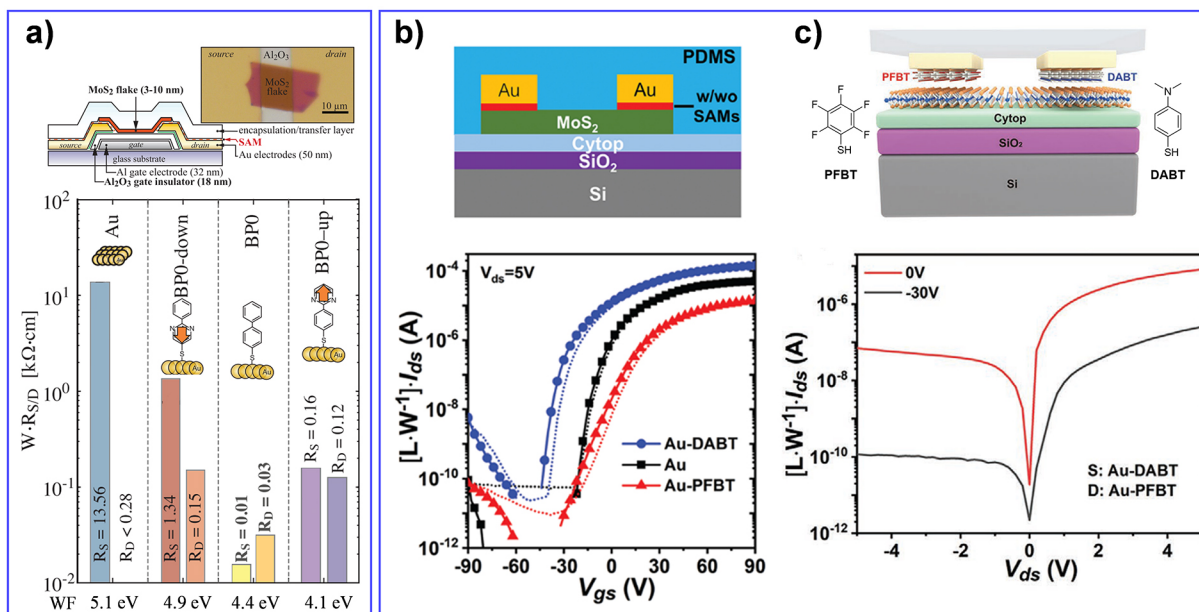


Figure 2. Molecular functionalized electrodes in TMD-FETs with (a) bottom-contact and (b,c) top-contact configurations. (a) Bottom-contact MoS₂ FETs with SAMs functionalized electrodes and their contact resistances with/wo SAMs functionalization (W is the channel width. R_S and R_D are the contact resistances on the source and drain electrode sides, respectively). (b-c) Top-contact MoS₂ FETs with (b) symmetric and (c) asymmetric SAMs functionalized source and drain electrodes as well as corresponding electrical curves. Adapted with permission from refs 26 and 1. Copyright 2020 The Authors. Published by Wiley under a Creative Commons Attribution 4.0 International (CC BY 4.0) license.

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2.2 Molecular Functionalization of Top-Contact Electrodes

To date, most reports on functionalized source and drain electrodes have focused on FETs in a bottom-contact configuration. Conversely, top-contact FETs enables more efficient charge injection due to several geometric factors: in the former, injection occurs from the contact edge into the semiconductor, while in the latter, the entire contact area facing the gate can participate in the injection process^{24,29}. However, top-contact FETs face challenges with functionalization due to the typical deposition method of thermal evaporation.³⁰

Cho et al. engineered the interface between top-contact metal electrodes and MoS₂ using chemically adsorbed thiol molecules, which enhanced contact properties and improved carrier injection by lowering activation energies³¹. In 2022, our group developed a novel contact engineering approach to functionalize gold electrodes in top-contact FETs through a dry transfer strategy of chemically pre-modified electrodes¹. By functionalizing Au electrodes with appropriate electron-donating or withdrawing molecules, we could significantly regulate the device performance by altering the SHB between the electrode and the semiconductor (Figure 2b). Additionally, asymmetric functionalization of the source and drain electrodes with two different molecules having opposed dipole moments enabled the creation of high-performance Schottky diodes with a rectification ratio of approximately 10³ (Figure 2c). This advancement

substantially broadens the application scopes of molecular functionalization strategies in top-contact TMD-based FETs and establishes a foundation for developing high-performance TMD FETs for practical applications.

3 Molecular Engineering of TMD Semiconductor-Dielectric Interface

The interface between dielectric and semiconductor is crucial in FETs due to their extensive contact. This interface can be regulated using SAMs, allowing manipulation of the dielectric surface's properties such as surface energy and charge density. These alterations influence device performance by impacting the interface with the channel semiconductor, enhancing polarity effects, modifying the dielectric constant, and optimizing wetting characteristics and hydrophobic-hydrophilic balance³².

Unlike organic semiconductors, which utilize different terminal SAMs to control growth or orientation, TMD semiconductors have a fixed crystal structure, thus SAMs cannot alter structural orientation but can be chosen with functional end groups to dope the channel semiconductor. This doping shifts the Fermi level and controls the carrier concentration, thereby influencing device performance.³³⁻³⁵ Figure 3a depicts the functionalization process of the SiO₂ dielectric layer using octyltrichlorosilane (OTS), 3-(trimethoxysilyl)-1-propanamine (APTMS) and trichloro(1H,1H,2H,2H perfluorooctyl)silane (FOTS). Electrical results demonstrate that APTMS, which contains electron-donating groups, can n-dope MoS₂ FET and enhance performance, whereas FOTS, with electron-withdrawing groups, can p-dope

MoS₂ FET and reduce performance (Figure 3b). Additionally, doping effect diminishes as MoS₂ thickness increases (Figure 3c)³³. Xu et al. observed that octadecyltrimethoxysilane (OTMS) functionalization of the SiO₂ substrate significantly reduced the charged impurity density of MoS₂ FET, thereby enhancing mobility by an order of magnitude compared to that on untreated substrates³⁶. Najmaei et al. demonstrated that by varying the end functional groups in SAMs on SiO₂ one can finely tune electrical properties³⁷. These findings confirm that an appropriate molecular-engineered dielectric interface can be instrumental to optimize the performance of TMD FETs.

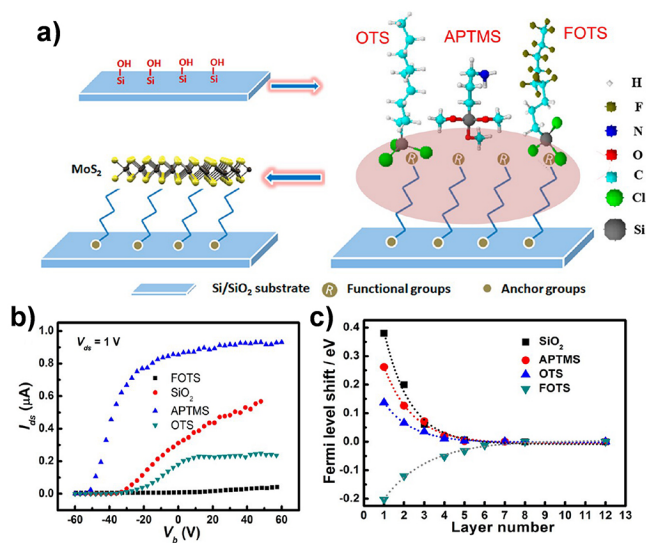


Figure 3. (a) Process of functionalization of the SiO₂ dielectric interface using OTS, APTMS and FOTS. (b) Transfer curves of MoS₂ FETs on various SAMs functionalized SiO₂ substrates. (c) The Fermi level shift of MoS₂ on various SAMs functionalized SiO₂ substrates as a function of the MoS₂ layer number. Adapted with permission from ref 33. Copyright 2013 American Chemical Society.

4 Molecular Engineering of TMDs Semiconductor-Environment Interface

In the bottom-gate configuration of TMDs FET (Figure 1a,1b), the large exposed area of the TMDs to the environment and its 2D ultrathin nature render the interface highly sensitive to environmental changes, establishing it as an ideal platform for investigating new functionalities such as charge doping, sensing of chemical analytes, light-responsiveness in molecularly functionalized devices, etc. Molecules can dope semiconductors by introducing functional groups or dopants, conferring various functionalities like photoresponse,³⁸⁻⁴² electrochemical modulation,^{3,43} chemical sensing,^{44,45} and enhancement of the hydrogen evolution reaction⁴⁶ etc. Electron-donating or electron-withdrawing groups in molecules can achieve the semiconductor doping through charge transfer or dipole induction, thereby increasing carrier concentration and mobility^{47,48}. This approach has improved FET performance, including lowering the threshold voltage and increasing the on-current. Molecules can be interfaced to the surface of 2D materials using different types of interactions, from the more weak physical adsorption onto the TMDs surface via van der Waals (vdWs) interactions to the more robust covalent bonding⁴⁹, both fostering efficient interactions between the molecule and the TMDs.

4.1 Noncovalent Functionalization of TMDs Surface

The atomically flat surface of TMDs offers an opportunity for noncovalent functionalization, as a tool to controllably adjust the physical and chemical properties of TMDs without

compromising their crystal structure, thereby preserving their outstanding optoelectronic properties⁵⁰. Noncovalent functionalization involves the formation of assemblies through the physical adsorption of molecules on the TMDs surfaces via vdWs or π - π interactions²⁸. This method can effectively control the doping level of TMDs and introduce new functionalities when functional molecules are employed, such as photo-switchable molecules or those with redox-active centers. In 2019, our group unveiled the impact of small aromatic solvent molecules on the optical and electrical properties of MoS₂ and black phosphorus (BP) (Figure 4)^{51,52}. Depending on the nature of the physisorbed molecule, the precise description of the molecule-TMD interactions can be achieved by considering dipoles and quadrupoles.

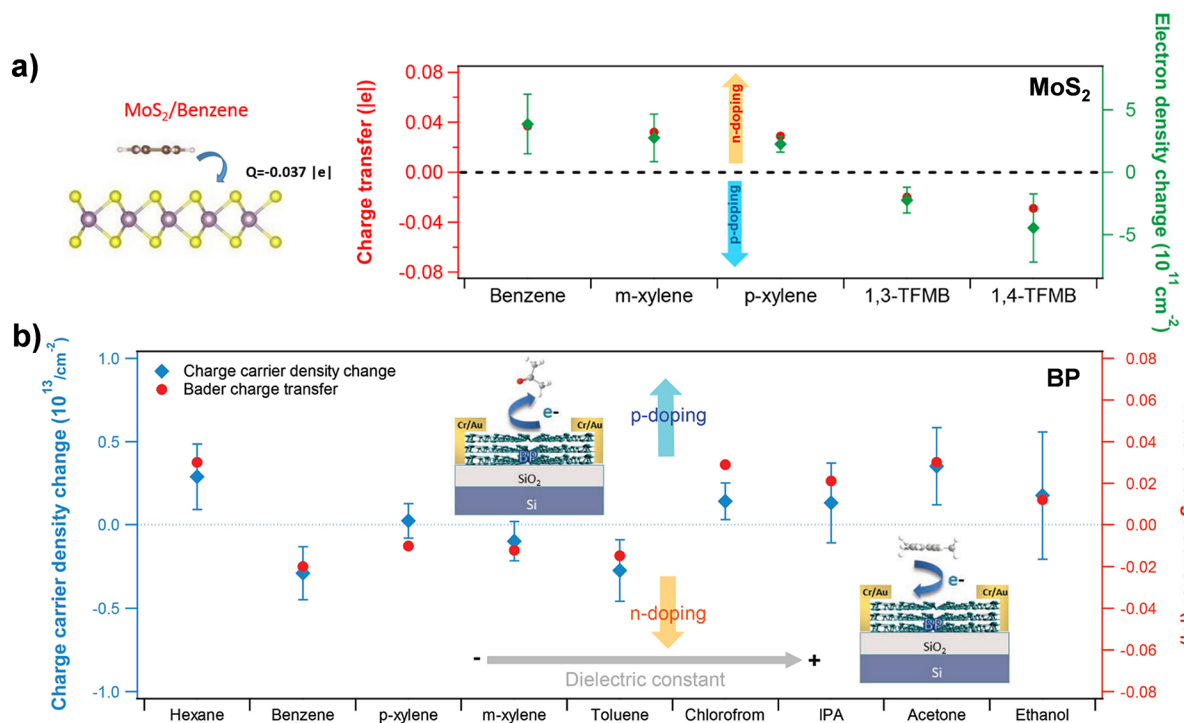


Figure 4. Noncovalent functionalization of molecules on TMDs surface. Schematic diagram and the calculated Bader charge transfer and charge carrier density change after physisorption

of (a) aromatic molecule on MoS₂ FET⁵¹ and (b) solvent molecules on BP FET⁵². Adapted with permission from refs 51 and 52. Copyright 2019 American Chemical Society. Copyright 2019 Wiley-VCH Verlag GmbH & Co.

4.2 Covalent Functionalization of TMDs Surface

The dangling bond-free surface of TMDs is inert, complicating the process of covalent functionalization, which often requires harsh chemical reactions, such as click-chemistry based strategies, to graft molecules onto their surface. Nevertheless, the production of 2D TMDs rarely provides defect-free crystals. In truth, a variety of different structural defects can be found on the surface of TMDs including dislocations, substitutional or interstitial defects, grain boundaries, and vacancies due to the absence of one or more atoms in the lattice. The nature of the defect found on the 2D surface, its amount and distribution depend on the method employed to produce the 2D crystals and the fine experimental conditions⁴⁹. Among these defects, chalcogen atom vacancies are the most prominent ones due to their low vacancy formation energy. Such point vacancies can serve as highly reactive anchoring sites for functionalization with thiol molecules through the formation of covalent bonds.

Numerous defect engineering strategies have been developed to introduce “artificially” point defects in high-quality CVD or mechanically exfoliated TMDs, facilitating covalent functionalization that would otherwise be challenging due to the inert nature of their surfaces⁵³. During the molecule covalent functionalization process, the sulfur atoms from thiols

occupy vacancies left by chalcogen atoms in TMDs, simultaneously repairing and functionalizing the defects. These covalently grafted molecules can then be annealed at high temperatures to cleave the S-C bonds, thereby completing the defective lattice healing of TMDs⁵⁴. In 2017, our group demonstrated that defects could be introduced in mechanically exfoliated MoS₂ monolayers through ion-beam irradiation, followed by covalent functionalization with thiols (figure 5a)⁵⁵. Further studies revealed that selenium defects in monolayer tungsten diselenide (WSe₂) could also be covalently functionalized with thiols. Such a demonstration not only expands the electrical characteristics of the devices given the ambipolar nature of WSe₂ but it allows to exploit and manipulate the photoluminescence properties of WSe₂ (Figure 5b)⁵⁶. In liquid phase exfoliated TMDs the defects are mostly positioned at the edges of the flakes. In 2021, we present a novel molecular strategy that enhances the electrical properties of printed TMD FET devices. This approach utilizes dithiolated conjugated molecules to simultaneously heal sulfur vacancies in solution-processed TMDs and covalently bridge adjacent flakes, creating networks of covalently connected flakes, thus facilitating improved charge transport through the film. Field-effect mobility, I_{on}/I_{off} ratio, and switching time are all increased reproducibly by an order of magnitude³. This strategy holds huge potential for integrating molecular properties into TMD-based films by using molecules containing ad-hoc functional groups, opening perspectives for applications in multiresponsive devices.

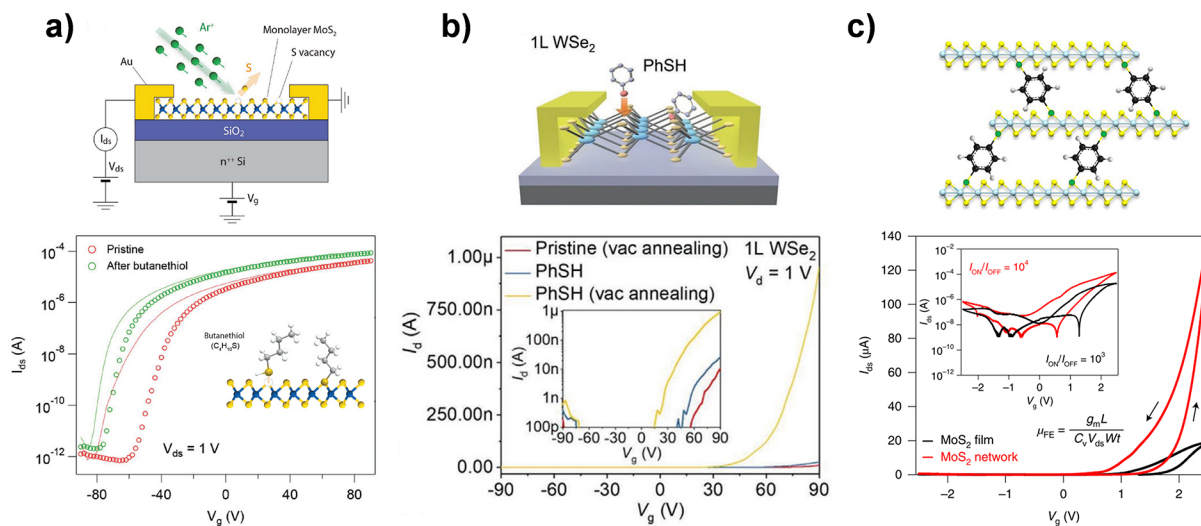


Figure 5. Covalent functionalization of molecules on TMD surface. (a) Scheme of the ion-bombardment irradiating and creating sulfur vacancies on MoS₂, as well as transfer curves before and after functionalization. (b) Scheme of WSe₂ FET with covalent functionalization of thiophenol molecules and transfer curves before and after functionalization. (c) Scheme of benzenedithiol-bridged MoS₂ inter-flake network. Adapted with permission from refs 55 and 56. Copyright 2017 and 2020 Wiley-VCH Verlag GmbH & Co. Reproduced with permission from ref 3. Copyright © 2021, The Author(s), under exclusive licence to Springer Nature Limited.

Overall, molecular engineering of the semiconductor-environment interface in TMD FETs offers a promising and versatile approach for developing high-performance electronic and optoelectronic devices characterized by enhanced efficiency, stability, and multifunctionality.

5 Application of Molecular Engineering in 2D Transition Metal Dichalcogenides

Molecular engineering has been demonstrated as a powerful tool to enhance various physical properties and introduce new functionalities in TMD electronics. By combining molecules with TMDs, this approach has progressed from enabling basic applications like carrier doping and chemical sensing to more advanced functionalities in devices such as responsiveness to optical and electrochemical inputs. Furthermore, it extends to proof-of-concept devices with complex functionalities, including memory devices, synaptic simulations, inverters, etc.

5.1 Carrier Doping

When a molecule is interfaced to a TMD semiconductor, the functional group of the molecule controls the doping effect on the TMD through charge transfer or dipole induction, thereby shifting the Fermi level and regulating carrier concentration and mobility in transistors. In 2019, we demonstrated that top surface functionalization of monolayer WSe₂ with electron-withdrawing trichloro(1H,1H,2H,2H-perfluorooctyl)silane (PFS) or electron-donating N[3-(trimethoxysilyl)propyl]ethylenediamine (AHAPS) SAMs is a viable route to control the polarity of WSe₂ FETs (Figures 6a,6b). An ambipolar FET with balanced electron and hole carriers was created by asymmetrically functionalizing the surface of a SiO₂ dielectric layer and a two-layer WSe₂ crystal with AHAPS and PFS SAMs, respectively (Figures 6c)². Recently, we showed that the interfacing via vdW interactions of 2D networks of strong electron-

donating cyanuric acid-melamine (CA-M) and covalent organic framework (COF) with monolayer MoS₂ is an efficient strategy to regulate carrier concentration across a broad range yielding device performance enhancement (figure 6d,6e)^{47,58}.

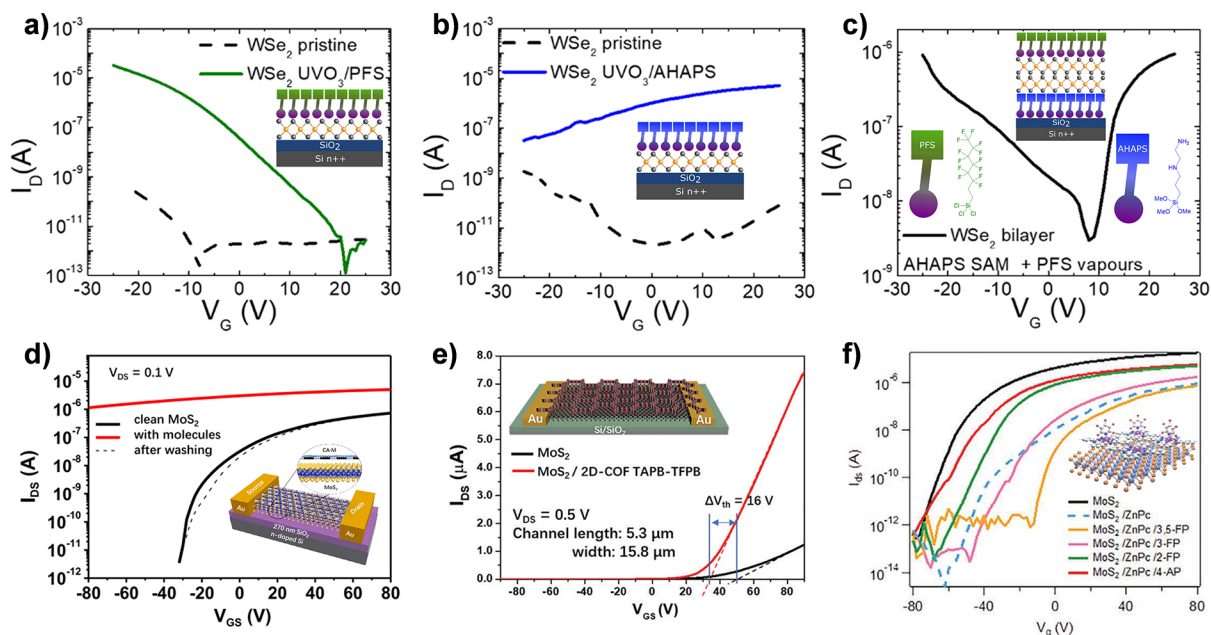


Figure 6. (a-c) Transfer curve of ozone-treated WSe₂ functionalized with PFS SAMs (a), AHAPS SAMs (b) and these two SAMs asymmetric functionalization (c), as well as corresponding architecture. (d-f) Transfer characteristics of MoS₂ FET functionalized with CA-M (d), TAPB-PDA COF (e) and ligand-coordinated ZnPc (f). Adapted with permission from refs 2, 47, 58 and 59. Copyright 2019 American Chemical Society. Copyright 2022 and 2023 The Authors. Published by Springer Nature and Wiley under a Creative Commons Attribution 4.0 International (CC BY 4.0) License. <https://creativecommons.org/licenses/by/4.0/>. Copyright 2020 Wiley-VCH Verlag GmbH & Co.

The functionality of molecules is not confined to a single molecular monolayer adsorbed onto the basal plane of the TMDs, but it can also be extended to a second layer grown over the first one thereby utilizing the 3D space above the TMD basal plane. Initially, we self-assembled a monolayer of metal phthalocyanine molecules on the monolayer MoS₂ surface, followed by the assembly of a second molecular layer through axial spatial coordination of the phthalocyanine metal core with pyridine exposing molecules possessing different dipoles. The results indicate that the second layer of molecules can effectively dope the TMD through dipole induction, allowing modulation of the carrier density up to $4.8 \times 10^{12} \text{ cm}^{-2}$ (figure 6f)⁵⁹. This approach demonstrates that TMD functionalization extends beyond the conventional 2D scope.

5.2 Chemical Sensor

The high sensitivity to the environment possessed by ultrathin TMD surfaces can be enhanced by molecular functionalization, rendering the hybrid system a powerful platform for chemical sensing. Proof-of-concept includes the detection of gases, isomers, both alkali and heavy metals, small organic compounds and biologically relevant molecules⁶⁰. In 2022, we revealed that defect healing in monolayer MoS₂ can be used to achieve remarkable sensitivities in the detection of highly carcinogenic polycyclic aromatic hydrocarbons (PAHs) (figure 7a)⁴⁵. Later, we further showed that defect-engineered MoS₂ can readily distinguish isomers⁵³ (figure 7b,7c) and detect heavy metal ions⁶¹ (figure 7d,7e) by observing changes in optical and electrical properties post-functionalization.

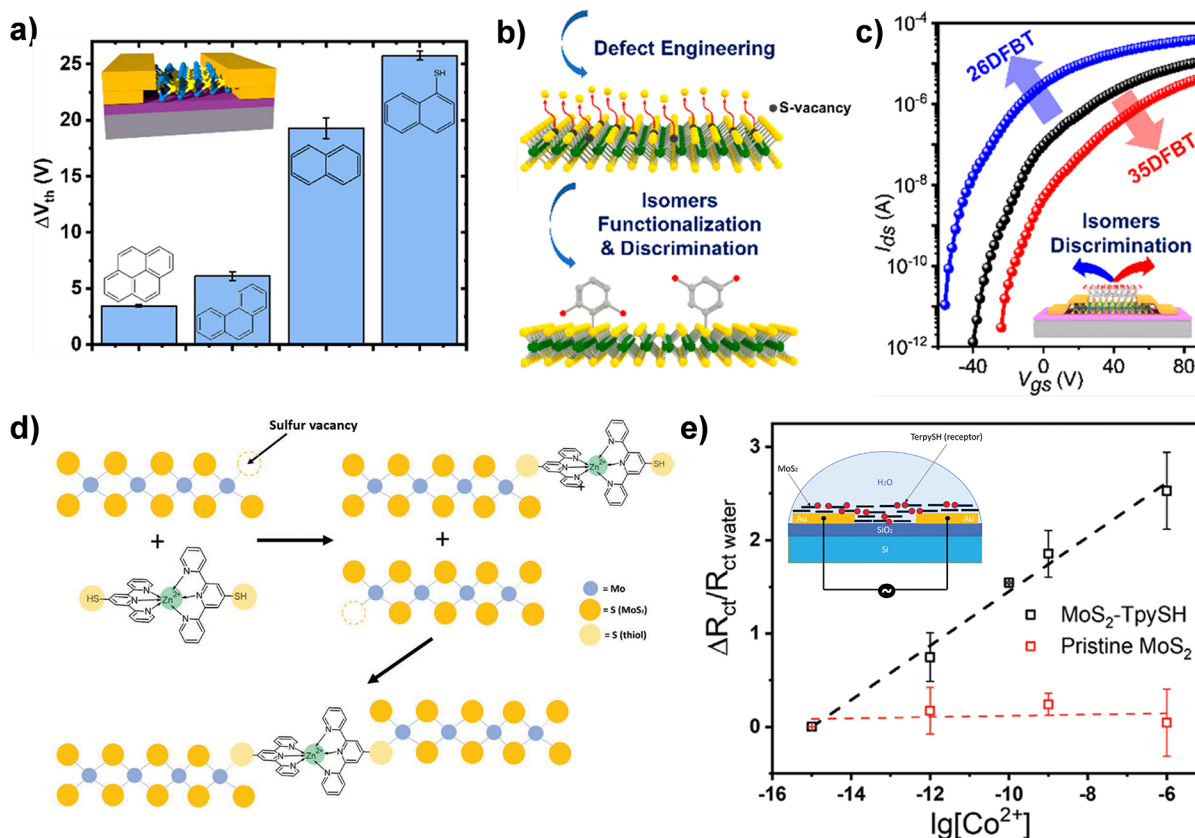


Figure 7. (a) Threshold voltage change as a function of the selected polycyclic aromatic hydrocarbons for MoS₂ FET. (b) Schematic illustration of the preparation steps for the isomer-functionalized MoS₂. (c) Transfer curves of monolayer MoS₂ FETs functionalized with isomers. (d) Schematic illustration of thiolated terpyridine molecules functionalized on MoS₂ surface. (e) The sensitivity (slope) comparison of pristine and functionalized MoS₂ device versus Co²⁺ concentration. Adapted with permission from refs 45, 53 and 61. Copyright 2022 and 2023 American Chemical Society. Copyright 2023 The Authors. Published by Wiley under a Creative Commons Attribution 4.0 International (CC BY 4.0) license.

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5.3 Electrochemical Switchable Device

When devices are functionalized with molecules containing redox-active centers, such as ferrocenes (Fc), tetrathiafulvalenes (TTF), and viologens, electrochemically switchable transistor devices can be constructed. These devices leverage the distinct electronic properties of the oxidized and reduced states of the molecules^{62,63}. Our experiments demonstrate that in a MoS₂ dual-gate FET functionalized with the ferrocene derivative 6-(ferrocenyl)hexanethiol (Fc-SH), both the reduced state (Fc) and oxidized state (Fc⁺) can be programmed by electrochemical stimuli using the top-gate voltage. The molecular layers of Fc and Fc⁺ induce different doping effects on MoS₂, with the process being reversible and regulated by the top gate. Moreover, the combination of redox molecules with ionic liquid (IL) endows the device with a steep subthreshold swing (SS) sub-60 mV/dec in the backward sweep⁴³. This research highlights the potential of combining TMDs with molecular engineering for developing electrochemically switchable functional devices with enhanced performance.

5.4 Light Switchable Device

Photoresponsive molecules represent a unique family of functional molecules that can undergo isomerization upon exposure to light at specific wavelength, resulting in isomers with distinct properties. This unique attribute enables the modulation of TMD performance via external light stimuli. In case such modulation is determined by the interfacing of molecules possessing different dipolar natures with MoS₂, the modulation can be boosted upon maximizing the

orientation of the molecules at the supramolecular level through the formation of a superlattice onto the 2D material. Within this context, we have pioneered the generation of highly ordered 2D molecular superstructures on highly oriented pyrolytic graphite (HOPG) and TMD surfaces^{64,65}.

Azobenzene (AZO) and spiropyran (SP) are photochromic molecules whose two states, achieved upon illumination with light at different wavelengths, display a significant difference in dipole moments, a characteristic that can be used to reversibly dope and undope the TMD through external light modulation. More precisely, AZO can reversibly switch between its *cis* (*cis*-AZO) and *trans* (*trans*-AZO) isomers, while SP can reversibly undergo photo-isomerization between the neutral SP and the zwitterionic merocyanine (MC) form, as shown in Figure 8d. Our research³⁹ demonstrates that upon illuminating at specific wavelengths the MoS₂ surface functionalized with AZO compounds it is possible to effectively and reversibly modulate both the carrier concentration and the optical properties of monolayer MoS₂, as depicted in Figure 8a-b. Figure 8c illustrates the device current response during one illumination cycle. Figure 8e-f display the enhanced electrical properties of SP-functionalized MoS₂ devices with graphene nanoribbons, achieving a photomodulation of the device current by 52% without signal attenuation across 10 cycles⁶⁶.

Diarylethene (DAE) is another type of photochromic molecule that can be reversibly toggled between open (DAE_o) and closed (DAE_c) isomers and upon light irradiation with UV and visible light. These two isomers possess distinct frontier orbital energy levels, enabling charge

transfer doping as depicted in Figure 8g. We functionalized the surface of few-layers thick WSe₂ using DAE, positioning the CB of WSe₂ between the lowest unoccupied molecular orbital (LUMO) of DAE_o and DAE_c. This configuration permits electron transfer from the CB of WSe₂ exclusively to the LUMO of DAE_c, but not to the LUMO of DAE_o. The electrical results, presented in Figure 8h, demonstrate device stability following 16 illumination cycles, as evidenced in Figure 8i³⁸.

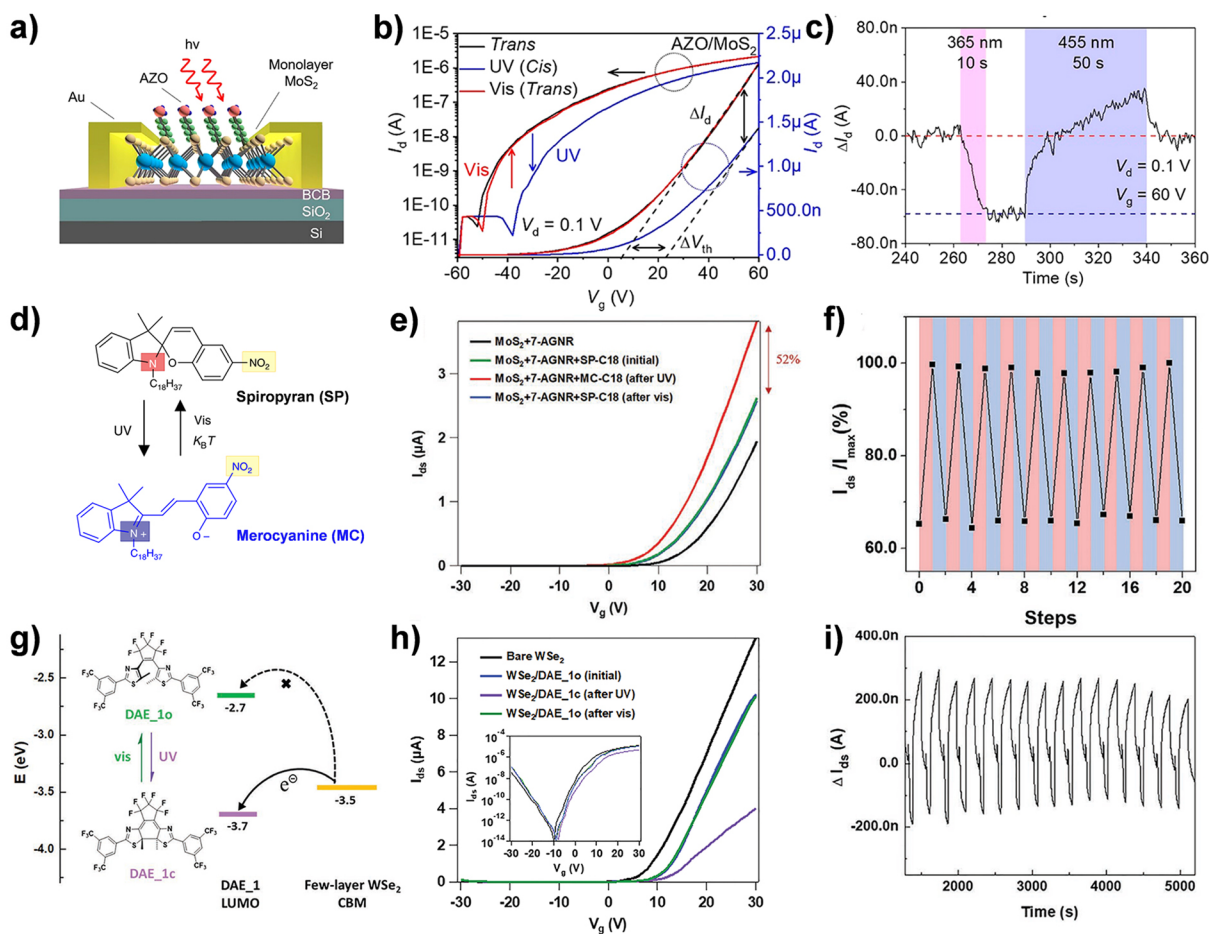


Figure 8. (a) Scheme of the MoS₂ FET with the physisorption of AZO molecules. (b) Transfer curves of the AZO/MoS₂ FET for one switching cycle (*trans-cis-trans* transition). (c) Time-

resolved photoresponse of AZO/MoS₂ FET when undergoing one cycle of UV and visible light irradiation. d) Chemical structure of the SP–MC derivative. e) Transfer curves of the MoS₂-Graphene-Nanoribbon device before and after SP-C18 molecules deposition and after UV–vis illumination. f) Current modulation with SP-C18 and MC-C18 isomers over ten illumination cycles of alternating UV and visible light irradiation. (g) Chemical structure of DAE_1 in its open and closed form and energy-level diagram. (h) Transfer curves of bare WSe₂, WSe₂/DAE_1 as prepared, and after UV–vis irradiation. (i) I_{ds}–time measurement under alternating dark and illumination conditions at V_g = 30 V and V_{ds} = 2 V over 16 illumination cycles. Adapted with permission from refs 39, 64, 66 and 38. Copyright 2019 American Chemical Society. Copyright 2018 The Authors. Published by Springer Nature under a Creative Commons Attribution 4.0 International (CC BY 4.0) License. <https://creativecommons.org/licenses/by/4.0/>. Copyright 2020 and 2019 Wiley-VCH Verlag GmbH & Co.

5.5 Multi-Responsive Device

Molecular engineering was previously introduced for individual interfaces in TMD electronic devices. To advance toward practical applications, this technique can be applied simultaneously at multiple interfaces to develop sophisticated analog functional devices. In particular, the functionalization of more than one interface using various stimulus-responsive molecules is extremely interesting for fabricating multilevel memory devices and artificial synapses. In 2021, we showcased a quaternary-responsive FET that was asymmetrically

functionalized on the top and bottom surfaces of a WSe_2 semiconductor with a ferroelectric layer (P(VDF-TrFE)) and a photoresponsive molecular SAM (SP), respectively (Figure 9a). This device responds to light, heat and electric stimuli as depicted in Figure 9. UV light illumination triggers the conversion of SP into MC, which can then be reverted to SP either by heat or visible light, resulting in an 84% modulation of current (Figure 9b). An electric field was then employed to induce the P(VDF-TrFE) reversible switch between its inherent polarizations, inducing a 99% change in current. Additionally, the synergistic use of light and electrical inputs was demonstrated to alter the WSe_2 from n-type to p-type, enabling the modulation of device polarity⁴¹. This multi-stimulus-responsive device significantly enriches TMD electronics functionality.

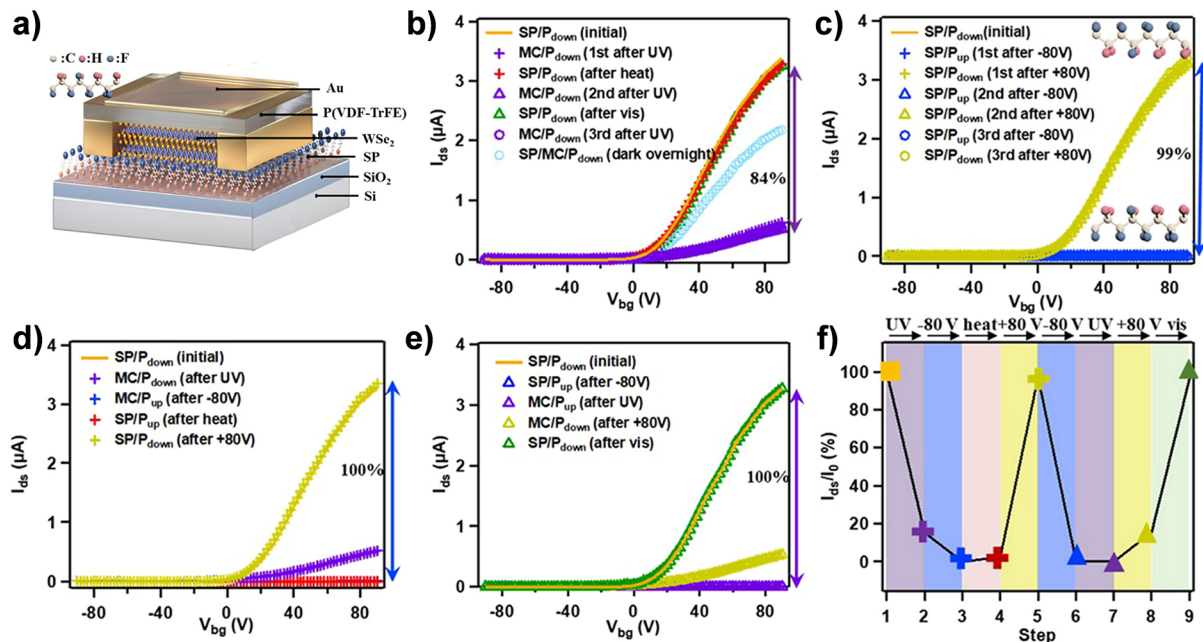


Figure 9. Molecularly engineered multiple stimulus-responsive devices. (a) Schematic illustration of the Janus SP/ WSe_2 /P(VDF-TrFE) FET device with the asymmetric

functionalization of the two faces of WSe₂: the bottom and top surface were functionalized with SP SAMs and a P(VDF-TrFE) layer, respectively. (b) Optical/thermal switching by UV and heat/vis/dark treatment. (c) Electrical switching by ± 80 V top-gate bias. (d) Orthogonal switching with the stimuli order of UV/ -80 V/heat/ $+80$ V and (e) -80 V/UV/ $+80$ V/vis. (f) Current modulation efficiency at $V_{bg} = 90$ V during the two switching cycles in (d) and (e). Adapted with permission from ref 41. Copyright 2021 American Chemical Society.

5.5.1 Memory

Photoresponsive molecules, with their two stable, switchable states, are ideally suited for memory applications in TMDs. In 2020, our group reported on DAE-functionalized few-layer WSe₂ devices designed for light-controllable memory. The photoisomerization of DAE led to a 97% modulation in hole current and a 52% modulation in electron current. By precisely controlling the light dose, we achieved 64 distinct levels of hole and electron currents, as shown in Figure 10b and 10c, corresponding to a data storage capacity of 7 bits⁶⁷. Subsequently, our group introduced the asymmetric functionalization of the top and bottom interfaces of few-layer WSe₂ with a ferroelectric P(VDF-TrFE) layer and a photoresponsive DAE layer, respectively. This design enabled a multi-level memory with dual electric field and optical control, detailed in Figure 10d-f. The synergistic modulation of optical and electric fields resulted in an output current modulation efficiency of up to 87%. The device encompasses a total of 9 ferroelectric states and 84 optical states, combining to offer 756 distinct resistive

states. It also maintains cyclic endurance of more than 10 cycles and a retention time exceeding 1000 hours⁴.

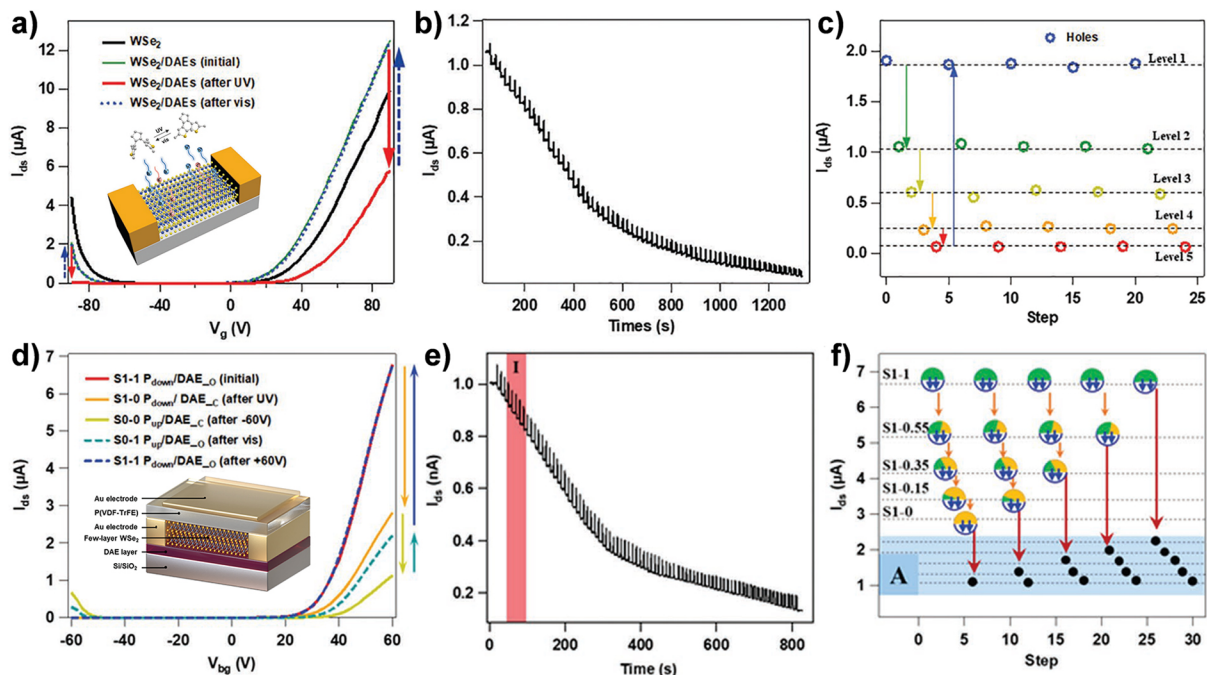


Figure 10. (a-c) Memory composed of a single molecularly engineered interface. (a) Transfer curves of pristine WSe_2 and WSe_2/DAE blend as prepared and after UV-vis irradiation. (b) Dynamic hole current I_{ds} -time curves under periodic UV irradiation per 20 s enabling to achieve in total 64 levels. (c) The five distinct current levels over five illumination cycles recorded at $V_g = -90$ V. (d-f) Memory composed of asymmetric functionalization of the WSe_2 surfaces with different (macro)molecular functions. (d) Transfer curves of DAE/ WSe_2 /FeFET by alternating UV/vis irradiation and ± 60 V bias. (e) Dynamic I_{ds} current evolution behavior under exposure to short UV pulses at $V_{bg} = 0$ V, enabling to achieve 84 distinct current levels. (f) The multilevel current of DAE/ WSe_2 /FeFET device over five cycles by different stimuli

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5.5.2 Artificial Synapses

The multi-interfaces molecular engineering in TMDs is a facile route to realize devices capable to respond to multiple stimuli, by dynamically adjusting the carrier density. This approach also offers a unique opportunity to emulate artificial synapses by simulating both short-term potentiation (STP) and long-term potentiation (LTP). Recently, our group focuses on the molecular engineering of multiple interfaces to develop artificial synapses using a novel Janus 2D TMD⁶⁸. By asymmetrically dressing the two surfaces of MoS₂ with an electrochemically-switchable ferrocene (Fc)/ferrocenium (Fc⁺) redox couple and an optically-responsive photochromic azobenzene (AZO) derivative in vertical configuration electrochemical FET device, we could demonstrate a sophisticated control over synaptic memory functions (Figure 11). The functional complexity of the artificial synapse is harnessed through the integration of multiple materials as active components, enabling the encoding of both STP and LTP in a single device. The interplay of electrochemical and optical stimuli at the interface allows for the modulation of conductivity and memory states, showcasing the potential for high-density integration, energy efficiency, and fast data manipulation in brain-like computing. This innovative approach to interface functionalization opens up new avenues for the design of advanced neuromorphic devices with enhanced performance and versatility.

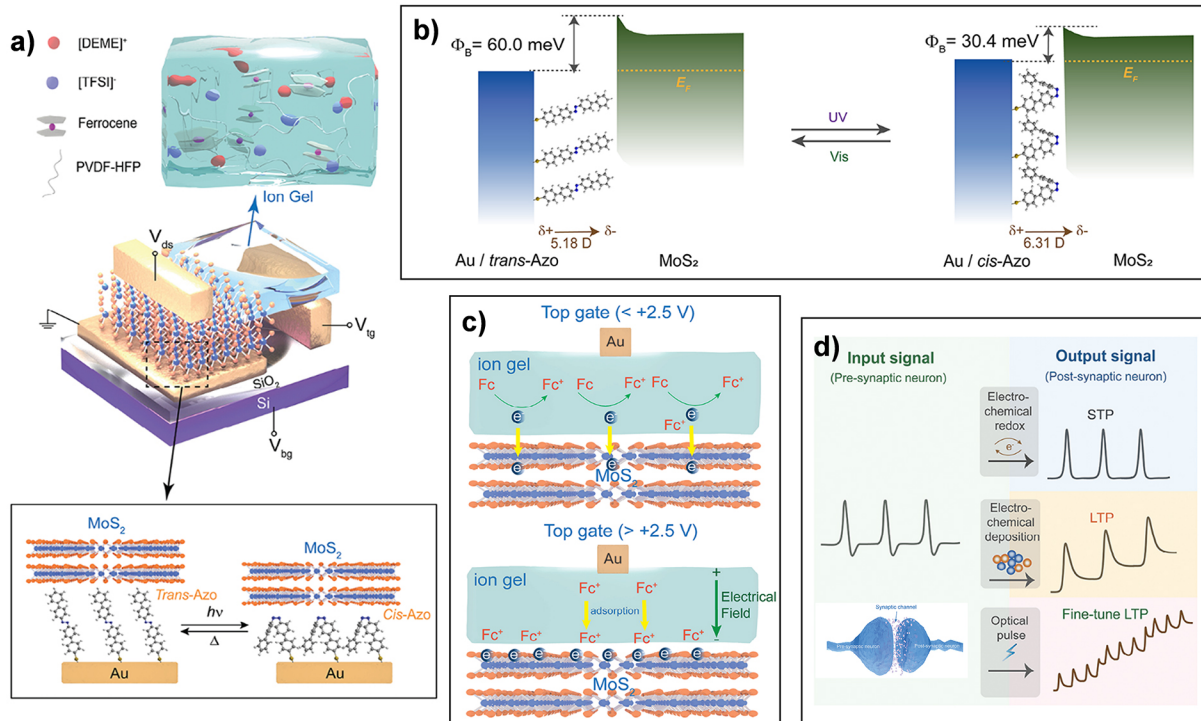


Figure 11. (a) Schematic representation of device structure of Janus Fc/MoS₂/Azo. (b) Band alignment of Au-Azo and MoS₂. (c) Scheme of electrochemical charge transfer between ferrocene/ferrocenium and MoS₂ and adsorption of ferrocenium. (d) Mechanism of STP, LTP, and finely tuned LTP synaptic signal formation from Janus Fc/MoS₂/Azo by electrochemical and optical inputs. Reproduced from ref 68. Copyright 2023 The Authors. Published by Wiley under a Creative Commons Attribution 4.0 International (CC BY 4.0) license.

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5.6 Logic Inverter

The realization of logic circuitries is a significant goal in current research on 2D materials for electronic applications. Interface molecular engineering represents an effective tool for the

construction of TMDs-based logic circuits. The functionalization with specific molecules of the TMD surface makes it possible to modify its electronic properties, thereby enabling device polarity modulation. This is critical for designing advanced electronics, especially logic inverters, which rely on switching stably between high and low output states in response to an external input. In 2019, Ji et al. functionalized CVD-grown WSe₂ by selecting electron-donating or electron-withdrawing molecules, in which, diethylenetriamine (DETA) functionalization was used to realize NMOS, and 4-nitrobenzenediazotetrafluoroborate (4-NBD) functionalization was employed to tailor PMOS, achieving controlled doping and polarity modulation (Figure 12a,b). This enabled the integration of chemically tuned FETs into complementary metal-oxide-semiconductor (CMOS) inverters, showcasing extremely low energy consumption with a maximum V_{gain} of 10 and power consumption around 0.17 nW (Figure 12c–d) ⁴².

Additionally, incorporating optical switching molecules into the TMD structure provides a means to dynamically adjust inverter performance through light-induced reversible changes in electrical properties. These molecules can change their conductive properties upon exposure to light, allowing the inverter to respond dynamically to optical stimuli. In 2021, we studied the integration of photoswitching molecules on 2D TMDs to enhance inverter performance⁴². This was made possible through the functionalization of MoS₂ with 3D axial coordination using AZO photochromic molecules, via the fine control of light programmable logic inverter (Figure 12e-g). Upon UV irradiation to trigger the isomerization of AZO to the *cis* state, the

voltage at the transition point is reduced by half. This optical control represents a major step forward as it enhances the versatility and responsiveness of TMD-based inverters, providing rapid on/off switching that is key for efficient logic operations. The addition of light-responsive functionality not only expands the potential applications of TMD inverters in optoelectronics but also contributes to the development of more energy-efficient and miniaturized digital circuits.

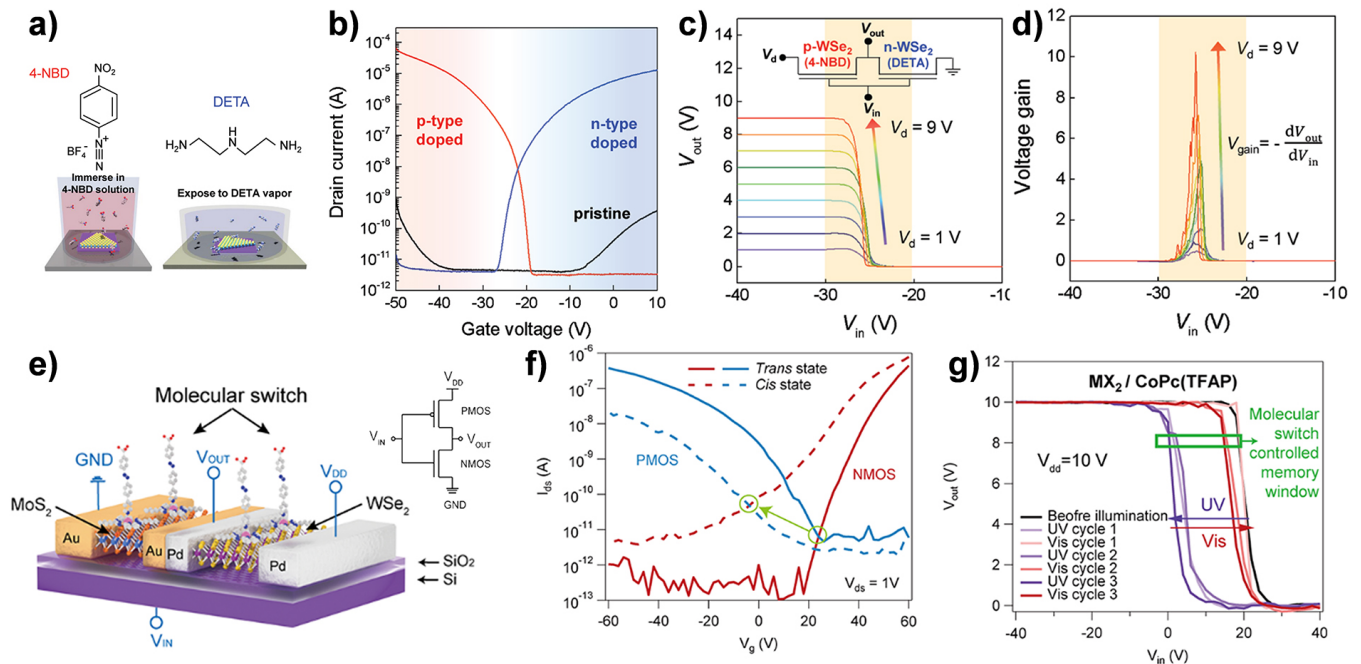


Figure 12. (a) Chemical doping processes using 4-NBD and DETA molecules for p- and n-type doping, respectively. (b) Transfer characteristics of pristine and doped WSe₂ FET devices. (c) V_{out}-V_{in} and (d) voltage gain curves of the CMOS inverter. (e) Schematic representation and the circuit of the molecular functionalized inverter. (f) Transfer characteristics of NMOS and PMOS with the molecular switch on both *trans* state and *cis* state. (g) V_{out}-V_{in} of the inverter

and the dynamic cycles controlled by the molecular switch. Adapted with permission from ref 69 and 42. Copyright 2019 Wiley-VCH Verlag GmbH & Co. Copyright 2021 American Chemical Society.

6 Conclusion and Outlook

This Account provides a comprehensive assessment of molecular engineering across all interfaces of 2D TMD devices, elucidating the individual and synergistic effects that can be integrated into TMD FETs. This approach has proven vital for enhancing electronic and optoelectronic properties of TMDs. The precise manipulation of interfaces among electrodes, dielectrics, and semiconductors holds the potential for substantial device performance improvements and multifunctionality. Ongoing research is establishing molecular engineering as a pivotal methodology in advancing electronic device technology. Additionally, molecular functionalization of TMD surfaces enables the dynamic adjustment of electronic characteristics, thus facilitating the design of devices such as logic inverters, which are building blocks in digital circuits. Although the integration of functionalized FETs into basic logic circuits has been demonstrated, realizing more complex logic circuits for practical applications remains a significant challenge. Future developments are expected to focus on addressing major challenges, including: 1) Multi-responsive devices: Although single-stimuli responsive TMD devices are well-developed, multi-stimulus examples remain scarce but promising. The development of multi-stimuli-responsive molecular systems, which operate independently without interference from each other, has become a critical focus. 2) Analog neuromorphic

circuits: Employing TMD devices to simulate neural structures like synaptic devices may achieve biomimetic functionalities. However, current biomimetic devices remain isolated from actual neural networks. This gap may be bridged through optimized interface contacts, innovative device architectures, and improved synaptic learning behaviors. 3) Material and interaction optimization: Advancing the performance and functionalities of TMD devices necessitates optimizing molecular interactions and exploring new materials. It is vital to balance performance enhancements with the integration of new functionalities, ensuring that any added functional molecules do not detract from established performance metrics. 4) Large-area controllable molecular doping toward integration: Molecular functionalization is apt for expansive circuit applications, yet controlling device performance and polarity through molecular directional doping presents a challenge. This may be addressed by designing selective in-situ molecular assembly on TMD surfaces and tailoring molecular structures for selective doping and polarity control, essential for achieving NMOS and PMOS integration. 5) Device stability: Most TMDs are n-type semiconductors, thus are highly susceptible to water and oxygen exposure. This susceptibility significantly compromises the stability of TMD-based electronic devices. Protective strategies, such as encapsulation, are useful, though they can introduce unwanted doping. Thus, molecular engineering to shield devices from atmospheric exposure and investigating molecular interactions at interfaces are promising directions for enhancing device stability. Overall, the integration of molecular engineering with TMDs could revolutionize computing and data processing applications, significantly impacting various technological sectors.

AUTHOR INFORMATION

Corresponding Author

Paolo Samorì – *Université de Strasbourg, CNRS, ISIS UMR 7006, 8 allée Gaspard Monge, F-67000 Strasbourg, France*; orcid.org/00000001-6256-8281; E-mail: samori@unistra.fr

Authors

Bin Han – *Université de Strasbourg, CNRS, ISIS UMR 7006, 8 allée Gaspard Monge, F-67000 Strasbourg, France*; orcid.org/0000-0002-7672-2734;

Notes

Any additional relevant notes should be placed here.

Biographies

Bin Han is currently a postdoctoral researcher in the group of Prof. Paolo Samorì at the University of Strasbourg. He received his B.S. degree in chemistry from Heilongjiang University and his M.S. degree in chemistry from Tianjin University with Prof. Wenping Hu. Then he obtained his Ph.D. degree in chemistry from the University of Strasbourg in 2023 under the supervision of Prof. Paolo Samorì. His research primarily focuses on the molecular functionalization of 2D material devices.

Paolo Samorì is Distinguished Professor at the Université de Strasbourg, and Director of the Nanochemistry Laboratory. He is Member different national and international academies

including the European Academy of Sciences (EURASC), the Academia Europaea, the German National Academy of Science and Engineering (ACATECH), the French Académie des Technologies, His research interests include nanochemistry, supramolecular sciences, materials chemistry, with a specific focus on 2D materials and applications in optoelectronics, energy, and sensing.

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REFERENCES

- (1) Han, B.; Zhao, Y.; Ma, C.; Wang, C.; Tian, X.; Wang, Y.; Hu, W.; Samori, P. Asymmetric Chemical Functionalization of Top-Contact Electrodes: Tuning the Charge Injection for High-Performance MoS₂ Field-Effect Transistors and Schottky Diodes. *Adv. Mater.* **2022**, *34*, 2109445.
- (2) Stoeckel, M.-A.; Gobbi, M.; Leydecker, T.; Wang, Y.; Eredia, M.; Bonacchi, S.; Verucchi, R.; Timpel, M.; Nardi, M. V.; Orgiu, E.; Samori, P. Boosting and Balancing Electron and Hole Mobility in Single- and Bilayer WSe₂ Devices via Tailored Molecular Functionalization. *ACS Nano* **2019**, *13*, 11613-11622.
- (3) Ippolito, S.; Kelly, A. G.; Furlan de Oliveira, R.; Stoeckel, M.-A.; Iglesias, D.; Roy, A.;

- Downing, C.; Bian, Z.; Lombardi, L.; Samad, Y. A.; Nicolosi, V.; Ferrari, A. C.; Coleman, J. N.; Samorì, P. Covalently Interconnected Transition Metal Dichalcogenide Networks via Defect Engineering for High-Performance Electronic Devices. *Nat. Nanotechnol.* **2021**, *16*, 592–598.
- (4) Qiu, H.; Herder, M.; Hecht, S.; Samorì, P. Ternary-Responsive Field-Effect Transistors and Multilevel Memories Based on Asymmetrically Functionalized Janus Few-Layer WSe₂. *Adv. Funct. Mater.* **2021**, *31*, 2102721.
- (5) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666.
- (6) Manzeli, S.; Ovchinnikov, D.; Pasquier, D.; Yazyev, O. V.; Kis, A. 2D Transition Metal Dichalcogenides. *Nat. Rev. Mater.* **2017**, *2*, 17033.
- (7) Wang, S.; Liu, X.; Xu, M.; Liu, L.; Yang, D.; Zhou, P. Two-Dimensional Devices and Integration Towards the Silicon Lines. *Nat. Mater.* **2022**, *21*, 1225-1239.
- (8) Zhou, J.; Lin, J.; Huang, X.; Zhou, Y.; Chen, Y.; Xia, J.; Wang, H.; Xie, Y.; Yu, H.; Lei, J.; Wu, D.; Liu, F.; Fu, Q.; Zeng, Q.; Hsu, C.-H.; Yang, C.; Lu, L.; Yu, T.; Shen, Z.; Lin, H.; Yakobson, B. I.; Liu, Q.; Suenaga, K.; Liu, G.; Liu, Z. A Library of Atomically Thin Metal Chalcogenides. *Nature* **2018**, *556*, 355–359.
- (9) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-Layer MoS₂ Transistors. *Nat. Nanotechnol.* **2011**, *6*, 147-150.
- (10) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and Optoelectronics of Two-Dimensional Transition Metal Dichalcogenides. *Nat. Nanotechnol.* **2012**, *7*, 699-712.
- (11) Bian, Z.; Miao, J.; Zhao, Y.; Chai, Y. Strong Interlayer Interaction for Engineering Two-Dimensional Materials. *Acc. Mater. Res.* **2022**, *3*, 1220-1231.

- (12) Liu, Y.; Weiss, N. O.; Duan, X.; Cheng, H.-C.; Huang, Y.; Duan, X. Van der Waals Heterostructures and Devices. *Nat. Rev. Mater.* **2016**, *1*, 16042.
- (13) Casalini, S.; Bortolotti, C. A.; Leonardi, F.; Biscarini, F. Self-assembled monolayers in organic electronics. *Chem. Soc. Rev.* **2017**, *46*, 40-71.
- (14) Heimel, G.; Romaner, L.; Zojer, E.; Bredas, J.-L. The Interface Energetics of Self-Assembled Monolayers on Metals. *Acc. Chem. Res.* **2008**, *41*, 721-729.
- (15) Liu, Y.; Ji, D.; Hu, W. Recent progress of interface self-assembled monolayers engineering organic optoelectronic devices. *DeCarbon* **2024**, 100035.
- (16) Fu, Y.; Chen, J.; Sun, H.; Li, K.; Xu, W.; He, Q.; Facchetti, A.; Cheng, J. A facile approach for significantly enhancing fluorescent gas sensing by oxygen plasma treatments. *Sens. Actuators, B* **2021**, *331*, 129397.
- (17) Ulman, A. Formation and structure of self-assembled monolayers. *Chem. Rev.* **1996**, *96*, 1533-1554.
- (18) Shen, P.-C.; Su, C.; Lin, Y.; Chou, A.-S.; Cheng, C.-C.; Park, J.-H.; Chiu, M.-H.; Lu, A.-Y.; Tang, H.-L.; Tavakoli, M. M.; Pitner, G.; Ji, X.; Cai, Z.; Mao, N.; Wang, J.; Tung, V.; Li, J.; Bokor, J.; Zettl, A.; Wu, C.-I.; Palacios, T.; Li, L.-J.; Kong, J. Ultralow contact resistance between semimetal and monolayer semiconductors. *Nature* **2021**, *593*, 211-217.
- (19) Lindell, L.; Vahlberg, C.; Uvdal, K.; Fahlman, M.; Braun, S. Self-assembled monolayer engineered interfaces: Energy level alignment tuning through chain length and end-group polarity. *J. Electron. Spectrosc. Relat. Phenom.* **2015**, *204*, 140-144.
- (20) Marmont, P.; Battaglini, N.; Lang, P.; Horowitz, G.; Hwang, J.; Kahn, A.; Amato, C.; Calas, P. Improving charge injection in organic thin-film transistors with thiol-based self-assembled monolayers. *Org. Electron.* **2008**, *9*, 419-424.

- (21) Robin, M.; Harnois, M.; Molard, Y.; Jacques, E. Improvement of n-type OTFT electrical stability by gold electrode modification. *Org. Electron.* **2016**, *39*, 214-221.
- (22) Lampert, Z. A.; Barth, K. J.; Lee, H.; Gann, E.; Engmann, S.; Chen, H.; Guthold, M.; McCulloch, I.; Anthony, J. E.; Richter, L. J.; DeLongchamp, D. M.; Jurchescu, O. D. A simple and robust approach to reducing contact resistance in organic transistors. *Nat. Commun.* **2018**, *9*, 5130.
- (23) Fenwick, O.; Van Dyck, C.; Murugavel, K.; Cornil, D.; Reinders, F.; Haar, S.; Mayor, M.; Cornil, J.; Samori, P. Modulating the charge injection in organic field-effect transistors: fluorinated oligophenyl self-assembled monolayers for high work function electrodes. *J. Mater. Chem. C* **2015**, *3*, 3007-3015.
- (24) Natali, D.; Caironi, M. Charge Injection in Solution-Processed Organic Field-Effect Transistors: Physics, Models and Characterization Methods. *Adv. Mater.* **2012**, *24*, 1357-1387.
- (25) Li, M.; Liu, M.; Qi, F.; Lin, F. R.; Jen, A. K. Y. Self-Assembled Monolayers for Interfacial Engineering in Solution-Processed Thin-Film Electronic Devices: Design, Fabrication, and Applications. *Chem. Rev.* **2024**, *124*, 2138–2204.
- (26) Matković, A.; Petritz, A.; Schider, G.; Krammer, M.; Kratzer, M.; Karner-Petritz, E.; Fian, A.; Gold, H.; Gärtner, M.; Terfort, A.; Teichert, C.; Zojer, E.; Zojer, K.; Stadlober, B. Interfacial Band Engineering of MoS₂/Gold Interfaces Using Pyrimidine-Containing Self-Assembled Monolayers: Toward Contact-Resistance-Free Bottom-Contacts. *Adv. Electron. Mater.* **2020**, *6*, 2000110.
- (27) Li, J.; Wierzbowski, J.; Ceylan, Ö.; Klein, J.; Nisic, F.; Anh, T. L.; Meggendorfer, F.; Palma, C.-A.; Dragonetti, C.; Barth, J. V.; Finley, J. J.; Margapoti, E. Tuning the optical emission of MoS₂ nanosheets using proximal photoswitchable azobenzene molecules. *Appl. Phys. Lett.* **2014**, *105*, 241116.
- (28) Daukiya, L.; Seibel, J.; De Feyter, S. Chemical Modification of 2D Materials Using Molecules

and Assemblies of Molecules. *Adv. Phys. X* **2019**, *4*, 1625723.

(29) Shim, C.; Maruoka, F.; Hattori, R. Structural Analysis on Organic Thin-Film Transistor With Device Simulation. *IEEE Trans. Electron Devices* **2010**, *57*, 195-200.

(30) Haick, H.; Cahen, D. Contacting Organic Molecules by Soft Methods: Towards Molecule-Based Electronic Devices. *Acc. Chem. Res.* **2008**, *41*, 359-366.

(31) Cho, K.; Pak, J.; Kim, J.-K.; Kang, K.; Kim, T.-Y.; Shin, J.; Choi, B. Y.; Chung, S.; Lee, T. Contact-Engineered Electrical Properties of MoS₂ Field-Effect Transistors via Selectively Deposited Thiol-Molecules. *Adv. Mater.* **2018**, *30*, 1705540.

(32) Takeya, J.; Nishikawa, T.; Takenobu, T.; Kobayashi, S.; Iwasa, Y.; Mitani, T.; Goldmann, C.; Krellner, C.; Batlogg, B. Effects of polarized organosilane self-assembled monolayers on organic single-crystal field-effect transistors. *Appl. Phys. Lett.* **2004**, *85*, 5078-5080.

(33) Li, Y.; Xu, C.-Y.; Hu, P.; Zhen, L. Carrier Control of MoS₂ Nanoflakes by Functional Self-Assembled Monolayers. *ACS Nano* **2013**, *7*, 7795-7804.

(34) Cernetic, N.; Wu, S.; Davies, J. A.; Krueger, B. W.; Hutchins, D. O.; Xu, X.; Ma, H.; Jen, A. K. Y. Systematic Doping Control of CVD Graphene Transistors with Functionalized Aromatic Self-Assembled Monolayers. *Adv. Funct. Mater.* **2014**, *24*, 3464-3470.

(35) Lee, W. H.; Park, Y. D. Tuning Electrical Properties of 2D Materials by Self-Assembled Monolayers. *Adv. Mater. Interfaces* **2018**, *5*, 1700316.

(36) Wan, X.; Chen, K.; Xie, W.; Wen, J.; Chen, H.; Xu, J.-B. Quantitative Analysis of Scattering Mechanisms in Highly Crystalline CVD MoS₂ through a Self-Limited Growth Strategy by Interface Engineering. *Small* **2016**, *12*, 438-445.

(37) Najmaei, S.; Zou, X.; Er, D.; Li, J.; Jin, Z.; Gao, W.; Zhang, Q.; Park, S.; Ge, L.; Lei, S.; Kono, J.; Shenoy, V. B.; Yakobson, B. I.; George, A.; Ajayan, P. M.; Lou, J. Tailoring the Physical

Properties of Molybdenum Disulfide Monolayers by Control of Interfacial Chemistry. *Nano Lett.* **2014**, *14*, 1354-1361.

(38) Qiu, H.; Zhao, Y.; Liu, Z.; Herder, M.; Hecht, S.; Samorì, P. Modulating the Charge Transport in 2D Semiconductors via Energy-Level Phototuning. *Adv. Mater.* **2019**, *31*, 1903402.

(39) Zhao, Y.; Bertolazzi, S.; Samorì, P. A Universal Approach toward Light-Responsive Two-Dimensional Electronics: Chemically Tailored Hybrid van der Waals Heterostructures. *ACS Nano* **2019**, *13*, 4814-4825.

(40) Zhao, Y.; Ippolito, S.; Samorì, P. Functionalization of 2D Materials with Photosensitive Molecules: From Light-Responsive Hybrid Systems to Multifunctional Devices. *Adv. Opt. Mater.* **2019**, *7*, 1900286.

(41) Qiu, H.; Ippolito, S.; Galanti, A.; Liu, Z.; Samorì, P. Asymmetric Dressing of WSe₂ with (Macro)molecular Switches: Fabrication of Quaternary-Responsive Transistors. *ACS Nano* **2021**, *15*, 10668-10677.

(42) Wang, Y.; Iglesias, D.; Gali, S. M.; Beljonne, D.; Samorì, P. Light-Programmable Logic-in-Memory in 2D Semiconductors Enabled by Supramolecular Functionalization: Photoresponsive Collective Effect of Aligned Molecular Dipoles. *ACS Nano* **2021**, *15*, 13732-13741.

(43) Zhao, Y.; Bertolazzi, S.; Maglione, M. S.; Rovira, C.; Mas-Torrent, M.; Samorì, P. Molecular Approach to Electrochemically Switchable Monolayer MoS₂ Transistors. *Adv. Mater.* **2020**, *32*, 2000740.

(44) Urbanos, F. J.; Gullace, S.; Samorì, P. Field-effect-transistor-based ion sensors: ultrasensitive mercury(ii) detection via healing MoS₂ defects. *Nanoscale* **2021**, *13*, 19682-19689.

(45) Urbanos, F. J.; Gullace, S.; Samorì, P. MoS₂ Defect Healing for High-Performance Chemical Sensing of Polycyclic Aromatic Hydrocarbons. *ACS Nano* **2022**, *16*, 11234-11243.

- (46) Pak, S.; Lim, J.; Hong, J.; Cha, S. Enhanced Hydrogen Evolution Reaction in Surface Functionalized MoS₂ Monolayers. *Catalysts* **2021**, *11*, 70.
- (47) Wang, C.; Furlan de Oliveira, R.; Jiang, K.; Zhao, Y.; Turetta, N.; Ma, C.; Han, B.; Zhang, H.; Tranca, D.; Zhuang, X.; Chi, L.; Ciesielski, A.; Samorì, P. Boosting the Electronic and Catalytic Properties of 2D Semiconductors with Supramolecular 2D Hydrogen-Bonded Superlattices. *Nat. Commun.* **2022**, *13*, 510.
- (48) Wang, Y.; Wang, H.; Gali, S. M.; Turetta, N.; Yao, Y.; Wang, C.; Chen, Y.; Beljonne, D.; Samorì, P. Molecular Doping of 2D Indium Selenide for Ultrahigh Performance and Low-Power Consumption Broadband Photodetectors. *Adv. Funct. Mater.* **2021**, *31*, 2103353.
- (49) Ippolito, S.; Samorì, P. Defect Engineering Strategies Toward Controlled Functionalization of Solution-Processed Transition Metal Dichalcogenides. *Small Sci.* **2022**, *2*, 2100122.
- (50) Brill, A. R.; Kuntumalla, M. K.; de Ruiter, G.; Koren, E. Formation of Highly Ordered Self-Assembled Monolayers on Two-Dimensional Materials via Noncovalent Functionalization. *ACS Appl. Mater. Interfaces* **2020**, *12*, 33941-33949.
- (51) Wang, Y.; Slassi, A.; Stoeckel, M.-A.; Bertolazzi, S.; Cornil, J.; Beljonne, D.; Samorì, P. Doping of Monolayer Transition-Metal Dichalcogenides via Physisorption of Aromatic Solvent Molecules. *J. Phys. Chem. Lett.* **2019**, *10*, 540-547.
- (52) Wang, Y.; Slassi, A.; Cornil, J.; Beljonne, D.; Samorì, P. Tuning the Optical and Electrical Properties of Few-Layer Black Phosphorus via Physisorption of Small Solvent Molecules. *Small* **2019**, *15*, 1903432.
- (53) Han, B.; Gali, S. M.; Dai, S.; Beljonne, D.; Samorì, P. Isomer Discrimination via Defect Engineering in Monolayer MoS₂. *ACS Nano* **2023**, *17*, 17956-17965.
- (54) Yu, Z.; Pan, Y.; Shen, Y.; Wang, Z.; Ong, Z.-Y.; Xu, T.; Xin, R.; Pan, L.; Wang, B.; Sun, L.;

Wang, J.; Zhang, G.; Zhang, Y. W.; Shi, Y.; Wang, X. Towards intrinsic charge transport in monolayer molybdenum disulfide by defect and interface engineering. *Nat. Commun.* **2014**, *5*, 5290.

(55) Bertolazzi, S.; Bonacchi, S.; Nan, G.; Pershin, A.; Beljonne, D.; Samorì, P. Engineering Chemically Active Defects in Monolayer MoS₂ Transistors via Ion-Beam Irradiation and Their Healing via Vapor Deposition of Alkanethiols. *Adv. Mater.* **2017**, *29*, 1606760.

(56) Zhao, Y.; Gali, S. M.; Wang, C.; Pershin, A.; Slassi, A.; Beljonne, D.; Samorì, P. Molecular Functionalization of Chemically Active Defects in WSe₂ for Enhanced Opto-Electronics. *Adv. Funct. Mater.* **2020**, *30*, 2005045.

(57) Calavalle, F.; Dreher, P.; Surdendran, A. P.; Wan, W.; Timpel, M.; Verucchi, R.; Rogero, C.; Bauch, T.; Lombardi, F.; Casanova, F.; Nardi, M. V.; Ugeda, M. M.; Hueso, L. E.; Gobbi, M. Tailoring Superconductivity in Large-Area Single-Layer NbSe₂ via Self-Assembled Molecular Adlayers. *Nano Lett.* **2021**, *21*, 136-143.

(58) Wang, C.; Cusin, L.; Ma, C.; Unsal, E.; Wang, H.; Consolaro, V. G.; Montes-García, V.; Han, B.; Vitale, S.; Dianat, A.; Croy, A.; Zhang, H.; Gutierrez, R.; Cuniberti, G.; Liu, Z.; Chi, L.; Ciesielski, A.; Samorì, P. Enhancing the Carrier Transport in Monolayer MoS₂ Through Interlayer Coupling with 2D Covalent Organic Frameworks. *Adv. Mater.* **2023**, *36*, 2305882.

(59) Wang, Y.; Gali, S. M.; Slassi, A.; Beljonne, D.; Samorì, P. Collective Dipole-Dominated Doping of Monolayer MoS₂: Orientation and Magnitude Control via the Supramolecular Approach. *Adv. Funct. Mater.* **2020**, *30*, 2002846.

(60) Anichini, C.; Czepa, W.; Pakulski, D.; Aliprandi, A.; Ciesielski, A.; Samorì, P. Chemical Sensing with 2D Materials. *Chem. Soc. Rev.* **2018**, *47*, 4860-4908.

(61) Zhuravlova, A.; Ricciardulli, A. G.; Pakulski, D.; Gorczyński, A.; Kelly, A.; Coleman, J. N.;

Ciesielski, A.; Samorì, P. High Selectivity and Sensitivity in Chemiresistive Sensing of Co(II) Ions with Liquid-Phase Exfoliated Functionalized MoS₂: A Supramolecular Approach. *Small* **2023**, *19*, 2208100.

(62) Zhao, Y.; Gobbi, M.; Hueso, L. E.; Samorì, P. Molecular Approach to Engineer Two-Dimensional Devices for CMOS and beyond-CMOS Applications. *Chem. Rev.* **2022**, *122*, 50-131.

(63) Han, B.; Li, Y.; Ji, X.; Song, X.; Ding, S.; Li, B.; Khalid, H.; Zhang, Y.; Xu, X.; Tian, L.; Dong, H.; Yu, X.; Hu, W. Systematic Modulation of Charge Transport in Molecular Devices through Facile Control of Molecule–Electrode Coupling Using a Double Self-Assembled Monolayer Nanowire Junction. *J. Am. Chem. Soc.* **2020**, *142*, 9708-9717.

(64) Gobbi, M.; Bonacchi, S.; Lian, J. X.; Vercouter, A.; Bertolazzi, S.; Zyska, B.; Timpel, M.; Tatti, R.; Olivier, Y.; Hecht, S.; Nardi, M. V.; Beljonne, D.; Orgiu, E.; Samorì, P. Collective molecular switching in hybrid superlattices for light-modulated two-dimensional electronics. *Nat. Commun.* **2018**, *9*, 2661.

(65) Gobbi, M.; Galanti, A.; Stoeckel, M.-A.; Zyska, B.; Bonacchi, S.; Hecht, S.; Samorì, P. Graphene transistors for real-time monitoring molecular self-assembly dynamics. *Nat. Commun.* **2020**, *11*, 4731.

(66) Liu, Z.; Qiu, H.; Wang, C.; Chen, Z.; Zyska, B.; Narita, A.; Ciesielski, A.; Hecht, S.; Chi, L.; Müllen, K.; Samorì, P. Photomodulation of Charge Transport in All-Semiconducting 2D–1D van der Waals Heterostructures with Suppressed Persistent Photoconductivity Effect. *Adv. Mater.* **2020**, *32*, 2001268.

(67) Qiu, H.; Liu, Z.; Yao, Y.; Herder, M.; Hecht, S.; Samorì, P. Simultaneous Optical Tuning of Hole and Electron Transport in Ambipolar WSe₂ Interfaced with a Bicomponent Photochromic Layer: From High-Mobility Transistors to Flexible Multilevel Memories. *Adv. Mater.* **2020**, *32*,

1907903.

(68) Wang, Y.; Han, B.; Mayor, M.; Samori, P. Opto-Electrochemical Synaptic Memory in Supramolecularly Engineered Janus 2D MoS₂. *Adv. Mater.* **2023**, *36*, 2307359.

(69) Ji, H. G.; Solís-Fernández, P.; Yoshimura, D.; Maruyama, M.; Endo, T.; Miyata, Y.; Okada, S.; Ago, H. Chemically Tuned p- and n-Type WSe₂ Monolayers with High Carrier Mobility for Advanced Electronics. *Adv. Mater.* **2019**, *31*, 1903613.