

Light-programmable logic-in-memory in 2D semiconductors enabled by supramolecular functionalization: photoresponsive collective effect of aligned molecular dipoles

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ABSTRACT: Nowadays, the unrelenting growth of the digital universe calls for radically novel strategies for data processing and storage. An extremely promising and powerful approach relies on the development of logic-in-memory (LiM) devices through the use of floating gate and ferroelectric technologies to write and erase data in a memory operating as a logic gate driven by electrical bias. In this work, we report an alternative approach to realize the logic-in-memory based on two-dimensional (2D) transition metal dichalcogenides (TMDs) where multiple memorized logic output states have been established *via* the interfacing with responsive molecular dipoles arranged in supramolecular arrays. The collective dynamic molecular dipole changes of the axial ligand coordinated onto self-assembled metal phthalocyanine nanostructures on the surface of 2D TMD enables large reversible modulation of Fermi level of both *n*-type molybdenum disulfide (MoS₂) and *p*-type tungsten diselenide (WSe₂) field-effect transistors (FETs), to achieve multiple memory states by programming and erasing with ultraviolet (UV) with visible light, respectively. As a result, logic-in-memory devices were built up with our supramolecular layer/2D TMD architecture where the output logic is encoded by the motion of the molecular dipoles. Our strategy relying on the dynamic control of the 2D electronics by harnessing the functions of molecular-dipole-induced memory in a supramolecular hybrid layer represents a versatile way to integrate the functional programmability of molecular science into the next generation nano-electronics.

KEYWORDS. *two-dimensional material, molecular switch, azobenzene, transition metal dichalcogenides, logic-in-memory, supramolecular chemistry*

Information technologies, with their exponentially increasing demand of data manipulation, require a colossal number of computer units to fulfil efficient data processing and storage. The prevailing von Neumann architecture in computers is reaching a bottleneck where the computing and memory units are physically separated rising the concerns for energy-efficiency. Therefore, the in-memory computing is being optimized in order to meet the present requirements.¹⁻³ The engineering concept of logic-in-memory (LiM) devices relies on the incorporation of non-volatile memory units, *e.g.* floating gate and ferroelectric gate, in metal-oxide-semiconductor field-effect transistor (MOSFET) based logic gates.^{4,5} In these devices, either by charging-discharging or by electrical polarization, data are stored in the logic memory by electrically manipulating the control gate thereby modifying the magnitude of the current passing through the channel. While the electrical control for operating logic gates to impart memory functions is efficient, other approaches for memory writing and reading, such as those driven by optical stimuli, are also necessary to add functional diversification in logic-in-memory computing, in particular in extreme circumstances where optoelectronic memory is more facile to access.

One of the best solution to achieve such a goal is to realize optically controlled memory devices by using photochromic molecular switches.⁶⁻¹¹ The light-induced isomerization in photochromes can be used not only to amplify the functionality of materials in the form of work function tuning and reversible doping, but also allows such molecular switches to operate as active elements in memory manipulation.^{10, 12-17} Common photochromic molecules include azobenzene, diarylethenes, stilbene, spiropyrans and their derivatives. The simple chemical structures of the molecules make them convenient to be blended or chemically grafted on organic/polymer semiconductors, ensuring robust functionalization. Two-dimensional (2D) materials are a better “partner” for the molecular switches, in view of their extraordinary physical and chemical properties.^{18, 19} Among them, transition metal dichalcogenides (TMDs) are most studied semiconducting 2D materials with layer-dependent bandgap, high field-effect mobility and $I_{\text{on}}/I_{\text{off}}$ ratio. The variety of electronic properties of the TMD family makes them suitable components for building up *n*-MOSFET and *p*-MOSFET, which are key elements of binary logic devices. A number of organic molecules could be stably physisorbed on the atomically-thin, ultra-flat surface 2D TMDs by π - π stacking therefore inducing striking influences such as doping, forming van der Waals (vdW) heterostructures, *etc.*^{20, 21}

The most representative photochromic molecule, *i.e.* azobenzene, has been used to functionalize graphene and MoS₂ leading to improved exfoliation, enhanced photoresponse and light-controlled doping, emission tuning, *etc.*²²⁻²⁷ In particular, the reversible dipole-induced doping effect of azobenzene photoswitches, which modulates the threshold voltages and channel current dynamically by light stimuli, makes it an ideal system to establish optoelectronic memory on 2D logic devices.

Azobenzene molecules have been tethered to the surface of 2D materials either covalently or non-covalently. In the former case the functionalization unfortunately displays a low yield as a result of the limited reactivity of 2D materials with organic species. In the latter case, the azobenzenes are closely packed lying flat on the 2D surface, with the photoisomerization yield to some extent limited by steric hindrance. Moreover, within the films the dipoles display a moderate degree of structural order. As a result, the light-triggered magnitude of dipolar change at the ensemble level is not enough to ensure a large optoelectronic memory window on the 2D devices. An alternative strategy consists in using a molecular platform as a base with an anchoring point to control the patterning, thus positioning, of azobenzenes by placing them at ca. 1 nm far apart adopting an up-standing conformation.^{21, 28-30} More precisely, the distance between two adjacent azobenzenes is dictated by the lateral size of the platform, which is always much larger than the cross-section occupied by an up-standing azobenzene, thus the motion of azobenzenes is not sterically hindered by the adjacent photochromes and the photoswitching is expected to take place with a relatively high yield. Furthermore, if the vertically aligned azobenzenes all display the same orientation forming periodic structures, the photoswitching can be characterized by collective effects. The latter would enable to maximize the influence on the electronic properties of 2D materials underneath. Several previous works showed that triazatriangulenium (TATA) ions on surface could be an appropriate platform to bind azobenzene with ethynyl or phenyl spacers where the photoisomerization of freestanding azobenzene is observed by scanning tunnelling microscopy (STM).^{28, 31, 32} Recently, this class of molecule has been proved to enhance Raman signals and modulate the work functions of 2D materials.^{33, 34} However, production of the TATA platform requires a multistep cumbersome synthesis, whereas a thermodynamically driven approach based on molecular self-assembly would be more convenient. Among others, metal porphyrins and phthalocyanines are well-established molecular scaffolds that are usually flatly physisorbed on 2D materials, could also provide such functionality for growing axially bonded azobenzene ligands in a more versatile and modular manner.³⁵⁻³⁸ As we have previously demonstrated, the axial coordination of metal and functional pyridines is a viable route to generate vertical electrical field to monolayer MoS₂ thanks to different alignments and magnitudes of molecular dipoles (taking advantage of the confinement of crystal field of octahedral transition metal *d*-orbital of zinc and cobalt phthalocyanine).^{21, 39-41} The method has also been proved recently for stable growth of larger π -conjugated pyridinic ligands.⁴² Our previous observations revealed that the dipole-induced doping of axially-coordinated pyridines could attain 10¹²/cm² of charge carrier density change to MoS₂, being

comparable to traditional electron donor/acceptor molecules, ensuring a memory window of more than 20V on SiO₂ dielectric. Azobenzene molecules, whose molecular dipole could easily be tuned by photoisomerization, represent the best candidate for achieving collective dynamic doping on 2D materials. Therefore, in this work, we target the design of a molecular switch in which the azobenzene ligand is oriented perpendicular to the 2D surface. The molecular platform is used to template the azobenzene growth enabling the precise construction of optoelectronic memory of 2D logic devices operating through the collective effect of molecular dipoles that are controlled by light.

RESULTS

Our designed molecular switch is composed of a macromolecular metal complex, cobalt phthalocyanine, and a pyridinic ligand containing azobenzene (4-(4-((4-(trifluoromethyl)phenyl)diazanyl)phenyl)pyridine, denoted as TFAP, synthetic details see **Methods** and **Supporting Note 1 (Figure S1-S3)** in Supporting Information) as light responsive unit (**Figure 1a**). The UV-Vis absorption spectrum in chloroform shows the expected features for azobenzene derivatives with an intense band at 355 nm and broad low intensity band at 455 nm attributed to the π - π^* and n - π^* , respectively (**Figure S4c**). Ultra-performance liquid chromatography coupled to high resolution mass spectrometry (UPLC-HRMS) measurement revealed that the starting isomer is approaching 100% *trans*-TFAP (**Figure S4b**). The *trans* to *cis* photoisomerization of TFAP was studied upon irradiation of a diluted solution with a UV LED lamp ($\lambda_{\max} = 367$ nm, 2.4 mW cm⁻²). **Figure S4a** displays the variations of the light absorption due to the gradual transformation of the *trans* into the *cis* isomer. Notably, the band at 355 nm decreased while the band at 455 nm increases. Under the explored experimental conditions, the photo-stationary (UV-PSS) was reached after 12 min of irradiation. Then, the back isomerization to the *trans* isomer was fully achieved upon irradiation with a visible LED lamp ($\lambda_{\max} = 451$ nm, 2.1 mW cm⁻²). The photoswitching behaviour of the axial coordinated complex of TFAP ligand and CoPc (denoted as CoPc(TFAP)) is demonstrated in **Figure 1b** where both the Q (630-700 nm) band B band (300-400 nm) of CoPc, and the π - π^* band TFAP (350 nm) are presented with an association constant of 5857 M⁻¹ and 5941M⁻¹ in chloroform and DMSO, respectively (detailed titration spectra see **Supporting Note 2** in the Supporting Information). Similar to the photoswitching of TFAP, the π - π^* band decreased and n - π^* (455 nm) increased upon UV irradiation, and the absorption was recovered by irradiation with visible light. Time-dependent photoswitching is demonstrated in **Figure S7-S8** in the Supporting Information. Due to the overlap of the B band of CoPc and the π - π^* band of TFAP (which is in accordance with literature^{43, 44}), even at photostationary state both of their V_{th} shifts, a weak absorption at 300-400 nm has been observed. The Q band turned out being unaffected by the photoisomerization of TFAP, indicating the absence of electronic coupling between the two chromophores (**Figure S8**, Supporting Information).^{43, 45}

The complex photoswitching element at *trans* conformation intrinsically possesses a large molecular dipole moment whose magnitude is to a great extent determined by

the strong electron-withdrawing property of the $-\text{CF}_3$ group at the extremity of the TFAP ligand. The photoisomerization of the complex triggers the rotation/inversion of $\text{N}=\text{N}-\text{C}$ bond. The $-\text{CF}_3$ group is therefore brought closer to the 2D surface yielding to a shift of the molecular dipole direction. (**Figure 1c**). The modulation of the functional group distance and orientation brings to a distinct and collective change of the molecular dipole from +3.55 Debye (pointing out of the basal plane of MX_2) to -1.40 Debye (pointing towards the basal plane of MX_2) for MoS_2 and from +3.42 Debye to -1.58 Debye for WSe_2 , as shown in **Figure 1c**. Such large molecular dipoles act as a local electrical gate to

atomically-thin 2D material, introducing a decrease of the work function of MX_2 from 5.31 eV to 5.07 eV for MoS_2 , and from 4.66 eV to 4.27 eV for WSe_2 , as demonstrated in details in the DFT calculations in **Figure S9-S10**, Supporting Information. The shift of the work function could directly influence the drain-source current (I_{ds}) of the MOSFETs based on 2D MX_2 hence realizing program-read-erase process of the memory cell dynamically as driven by external light stimuli. Here, we demonstrate how the isomerization of the azobenzene could establish a memorized electrical output in the field-effect transistors (FETs) of both *n*-MOSFET and *p*-*MO*-

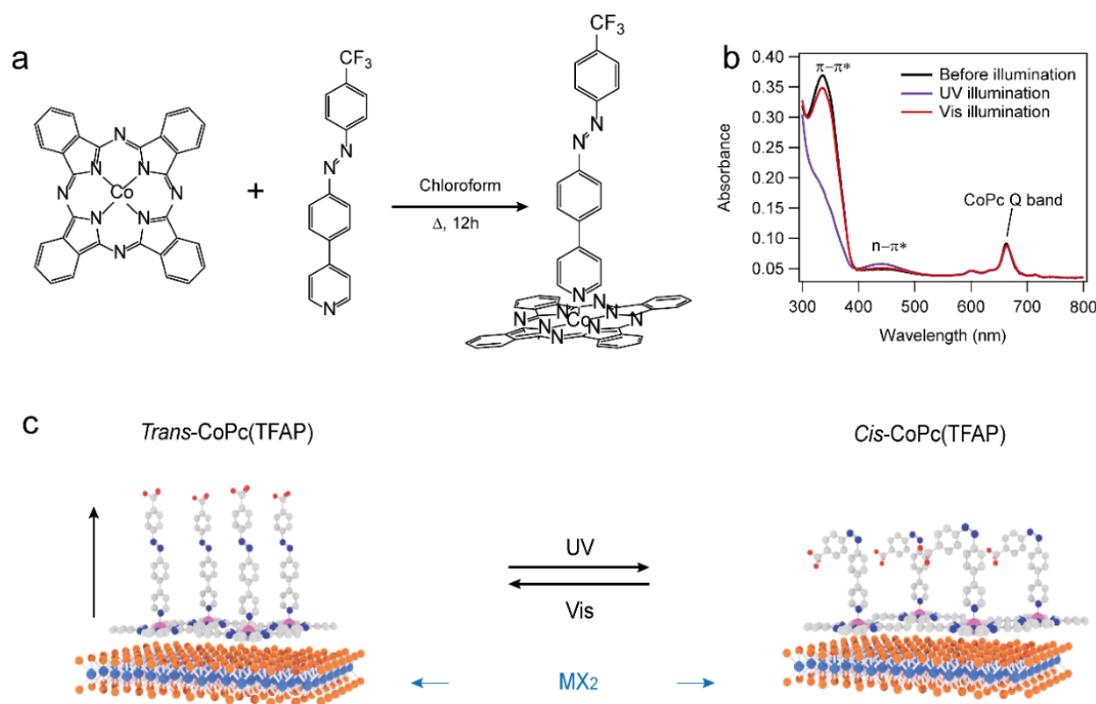


Figure 1. Light-induced motion of molecular switch on 2D surface. (a) Coordination of CoPc and photoswitchable TFAP ligand. (b) UV-Vis spectra of the switching of CoPc(TFAP) complex in chloroform. (c) Scheme of the *trans* and *cis* state molecular switch on MX_2 ($\text{M}=\text{Mo}, \text{W}$ and $\text{X}=\text{S}, \text{Se}$) surface controlled by light.

SFET of 2D TMDs, and be applied in light-programmable logic-in-memory NOR gate based on these 2D MOSFET, thus realizing dynamic electrical switch without fabricating complex circuitries.

Before elucidating how molecular switches could serve as optoelectronic memory units of binary inverters, we *first* evaluated the influence on the building blocks of binary inverters: *n*- and *p*-type MOS (NMOS and PMOS). Here we used monolayer MoS_2 and few-layer WSe_2 as NFET and PFET. Previous works from our group showed that optically-tunable molecular dipole enables to reversibly dope 2D TMDs by using light as remote control.^{26, 46-48} Inspired by these findings, we exploit our molecular switch as a dynamic doping remote control for MoS_2 and WSe_2 based transistor. We

adopt the two-step on-surface axial ligand growth strategy from our previous work which is critical for guaranteeing a maximized collective dipole growth out of the plane of 2D MX_2 (detailed information see **Figure S11**), as illustrated in **Figure 2a**.²¹ Unlike traditional approaches in the decoration of 2D materials with azobenzene switches which suffer from the incomplete photoswitching due to the dense packing on surface, the TFAP ligand in the complex is freestanding with large degree of conformational freedom for switching from *trans* to *cis* isomer thanks to the large planar molecular area and spacing dictated by the CoPc platform.^{31, 49-51} Such an edge-on geometry of the azobenzenes is also particularly suitable to manipulate the molecular dipoles in the direction perpendicular to the basal plane of the TMD surfaces, which

was proven to be the best orientation to boost the doping effect.^{46, 47} AFM images (**Figure S12** in the Supporting information) and XPS spectra (**Figure S13** in the Supporting information) provide evidence for the efficient coordination of TFAP ligand after the second step of functionalization. The resulting molecular-switch-functionalized MX₂ MOSFET is depicted in **Figure 2b**. A distinct *p*-doping is observed after each step of functionalization with a final charge carrier density shift of $4.38 \times 10^{12}/\text{cm}^2$ for MoS₂ and $2.40 \times 10^{12}/\text{cm}^2$ for WSe₂ (**Figure 2c** and **f**). In order to distinguish the doping caused by the light-induced charge transfer between CoPc and MX₂, and the doping from the photoswitching between the two states of the molecular switch, we conducted UV and Vis switching cycles for both the MX₂/CoPc heterostructure with and without the TFAP ligand. As demonstrated in **Figure 2d**, the illumination by

UV light induced a slight *p*-doping to MoS₂, corresponding to electron transfer from the conduction band of MoS₂ (4.1 eV) to the first reduction potential of CoPc (4.31 eV), while by illuminating with visible light, the electron transfer was not recovered through the cycles. Conversely, for WSe₂, with the major charge carrier being hole, we observed a slight irreversible photoinduced hole transfer from the valence band of WSe₂ (4.8 eV) to the first oxidation state of CoPc (5.5 eV) (**Figure 2g** and **Figure S14**, Supporting information). After adding the photoswitching ligand TFAP on MX₂/CoPc, as shown in **Figure 2e** and **h**, the light irradiation of the on-surface molecular switches determined a dynamic doping control window of averagely $(1.18 \pm 0.79) \times 10^{12}/\text{cm}^2$ for MoS₂ and $(2.18 \pm 0.15) \times 10^{12}/\text{cm}^2$ for WSe₂ (statistical analysis see **Figure S15** in the Supporting information).

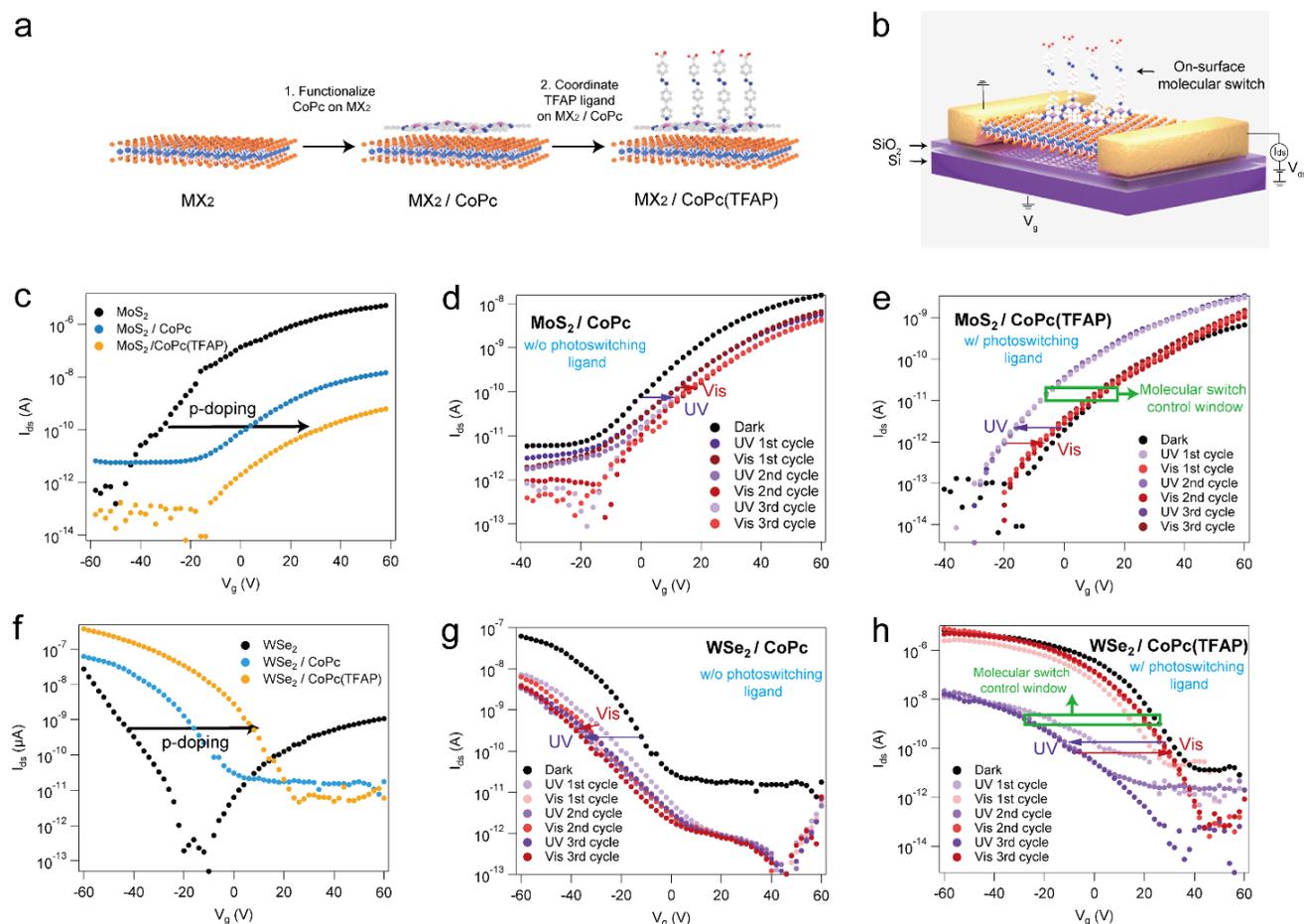


Figure 2. Molecular switch control over dynamic doping of MX₂ FET. (a) On-surface growth of molecular switch. **(b)** Device structure of MX₂ FET controlled by molecular switch. **(c)** I_d - V_g curve of MoS₂ FET before and after each step of molecular switch growth. **(d)-(e)** Photoswitching of the molecular switch on MoS₂ **(d)** before and **(e)** after the coordination with TFAP ligand. **(f)** I_d - V_g curve of WSe₂ FET before and after each step of molecular switch growth. The doping from the CoPc(TFAP) complex lead to pure *p*-type transport in WSe₂, compared to ambipolar characteristics in the initial state. **(g)-(h)** Photoswitching of the molecular switch on WSe₂ **(g)** before and **(h)** after the coordination with TFAP ligand.

The change in the orientation of the dipole moment upon isomerization from the *trans* state to the *cis* form occurring on an Avogadro number of molecules gives rise to a collective effect which is reflected in the major threshold voltage (V_{th}) shift upon light irradiation. The photoconductive and

the persistent photocurrent effect of MX₂ on SiO₂ dielectric is ruled out in our experiments, as demonstrated in control experiments carried out by fabricating graphene MOSFET which has no photoconductive effect due to the zero bandgap (**Figure S16-S17**, Supporting information).

Furthermore, we have observed an opposite V_{th} shift with pure TFAP ligand randomly physisorbed on the surface without any special confinement (**Figure S18**, Supporting information). The molecular switch controlled dynamic doping is also reflected in the optical properties of MoS_2 , as discussed in **Figure S19** in Supporting information. By and large, by remotely controlling with light the isomerization of the azobenzenes, one can fabricate transistors featuring a dynamic threshold voltage, which is beneficial for applications in smart electronics. According to the time-dependent photoswitching of TFAP ligand, the stepwise modulation of work function of MX_2 could be achieved by alternating the photoswitching time. As demonstrated in **Figure 3a**, multiple intermediate states between initial (denoted as “fully *trans* state”) and photostationary state (denoted as “fully *cis* state”) can be reached. Therefore, we could realize the programming of memory current by UV light with different irradiation time with the $\text{CoPc}(\text{TFAP})$ serving as a light-triggered “floating gate”. In **Figure 3b**, we track the time-dependent channel current at $V_g=0$ V of MoS_2 FET. The initial I_{ds} is in the 10^{-11} A scale, denoting the OFF state of the

transistor. Upon illumination for 1 min with UV light, the partial switching of TFAP ligand determines a negative shift of the threshold voltage and gives rise to an increase of the I_{ds} to 10^{-10} A. Upon longer irradiation times the I_{ds} further increases up to 10^{-8} A, demonstrating an extinction ratio of 10^3 . More precisely, it was possible to define 5 intermediate memory states programmed by 1 min, 2 min, 3 min, 5 min and 10 min. Conversely, as hole transport is dominant in WSe_2 FET, a decrease of channel current with the same UV light programming strategy was observed due to the negative shift of the threshold voltage (**Figure 3c**). The programmed memory current reaches the value of 10^{-9} A at $V_g=-60$ V compared to 10^{-7} A at initial state, showing an extinction ratio of 10^2 , hence being comparable to optoelectronic memories based on traditional floating gate technologies.⁵² The erase process could be accomplished by irradiating the FETs by visible light thus upon switching the TFAP from the *cis* back to the *trans* isomer. The photoswitching could also endure several program-erase cycles, as shown in **Figure 3d**.

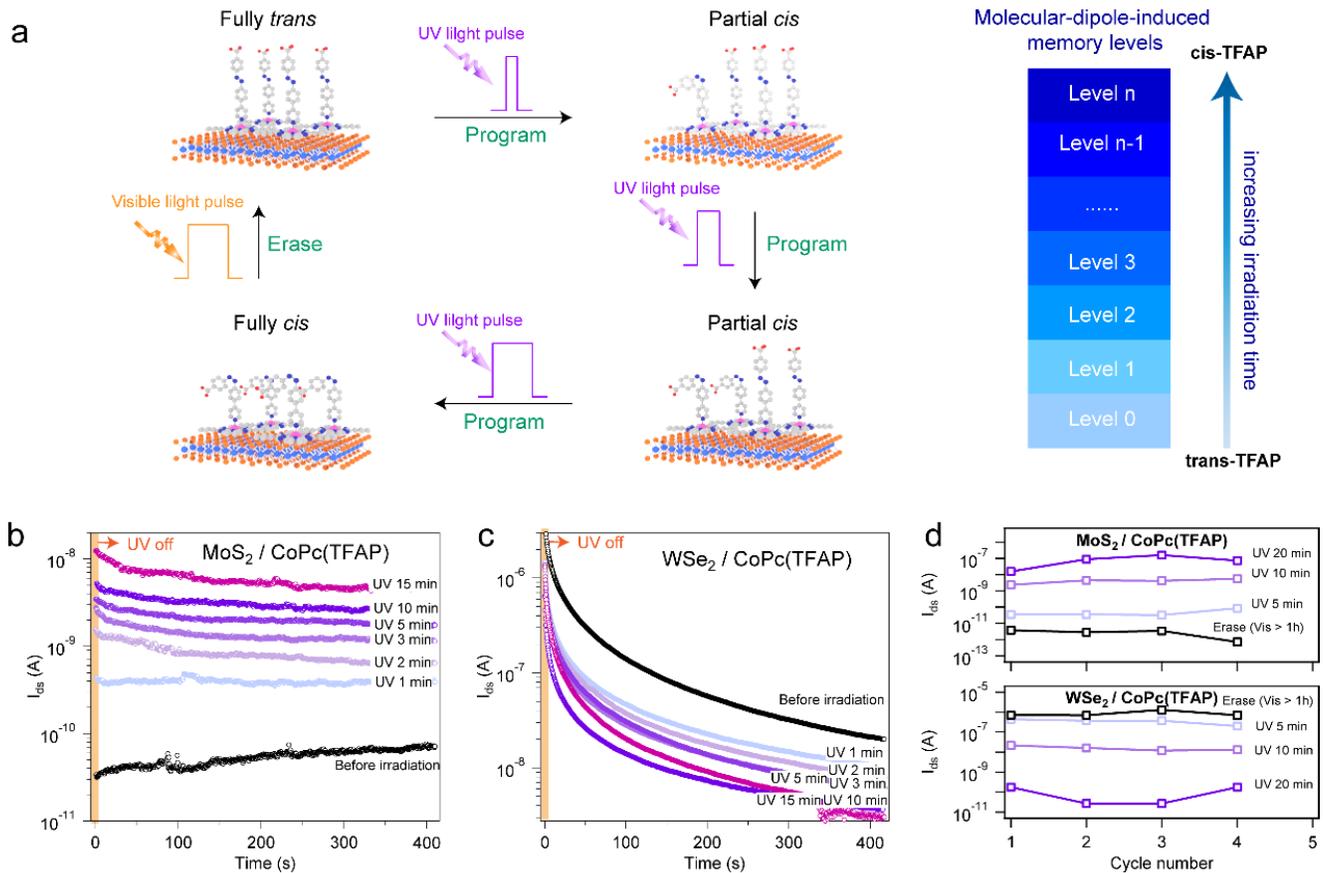


Figure 3. Time-dependent light programming and reliability of the photoswitching ligand on MoS_2 and WSe_2 FETs. **a**) Schematic representation of program-erase process by light pulses and multilevel control of memory states by axial photoswitching ligands. **b-c**) The retention curves of **b**) *n*-type MoS_2 ($V_g=0$ V, $V_{ds}=1$ V) and **c**) *p*-type WSe_2 ($V_g=-60$ V, $V_{ds}=1$ V) with various UV switching time. **d**) Channel current within program and erase cycles.

Based on previous discussions, our on-surface molecular switches could achieve dynamic control of threshold voltages by building optoelectronic memory window both on transistors of MoS₂ and WSe₂. It is essential to explore how they perform when these molecular-switch-controlled devices are embedded in electronic circuits. While the demand of data storage and simultaneous fast computing is rising dramatically during the recent years, logic-in-memory holds potential to become an important solution to energy-efficient computing for semiconductor industry. To address this challenge, we have built up a binary logic inverter (NOR gate) in which the MoS₂ and WSe₂ MOSFETs are in series in order to demonstrate a logic-in-memory device realized by molecular switches. The architecture and the electrical circuit, and the optical microscope image of the inverter are displayed in **Figure 4a** and **Figure S20a** in the Supporting information. Each MOSFET (NMOS being MoS₂ channel and PMOS being WSe₂ channel) exhibited unipolar transfer characteristics with $I_{on}/I_{off} > 10^5$ (**Figure 4b**) and both of their V_{th} shift negatively at *cis* state compared to *trans* state. The V_{out} versus V_{in} of the inverter is presented in **Figure 4c**

together with the gain shown in **Figure S20b** in Supporting information. The large dipolar doping from the *trans* conformation of molecular switch gave rise to the transition point appearing in the range of +18 V to +20 V, showing high-skewed inverter characteristics. While triggering the isomerization to the *cis* form, we could successfully adjust the transition point at $V_{dd}/2$ (5V), reaching the critical performance of an ideal inverter. This shift of the inverter transition point was found being fully reversible through UV-Vis illumination cycles, creating a memory window of 20V. Here, the molecular switch could be considered as a light-programmable “molecular switch floating gate” in which the readout of the inverter underneath could be programmed and erased upon irradiation at different wavelengths. The existence of the memory window of the inverter can be attributed uniquely to the motion of azobenzene unit on the TFAP ligand in the molecular switch. Conversely, in absence of the ligand, the inverter showed static transition point even with long illumination time (**Figure S21**, Supporting information). The shift was also found being time-dependent, according to the molecular kinetics of the TFAP ligand.

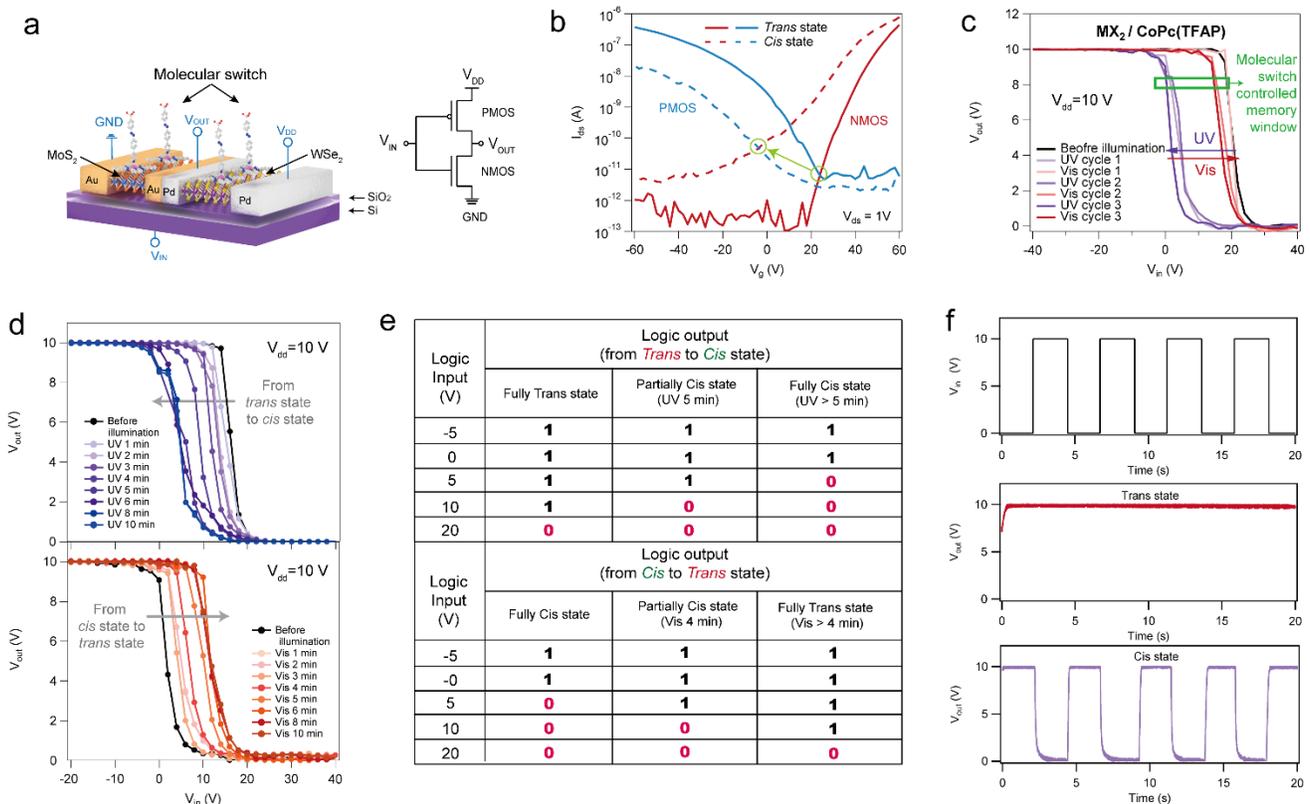


Figure 4. Molecular switch enabled light-programmable logic-in-memory device. (a) Schematic representation and the circuit of molecular switch controlled MoS₂-WSe₂ binary inverter. **(b)** Transfer characteristics of the *n*- and *p*- MOSFET with the molecular switch on both *trans* state and *cis* state. **(c)** V_{out} - V_{in} of the inverter and the dynamic cycles controlled by the molecular switch. The green circle indicates two distinctive transition point from different switch states. **(d)** V_{out} - V_{in} of the programmable dynamic switching point transition of the inverter controlled by illumination time on molecular switch. **(e)** Summary of the programmable dynamic logic output states by manipulating the molecular switch motion with UV and Vis illumination time. The measurement is done at $V_{dd}=10$ V. The logic output “1” corresponds to $V_{out}=10$ V and logic output “0” corresponds to $V_{out}=0$ V. **(f)** Time-dependent V_{out} of the inverter with V_{in} pulse cycles at *trans* and *cis* state of molecular switch showing distinct output signals in the two states. The *cis* state (metastable state) of molecular switch shows stability over gate electrical field.

As demonstrated in **Figure 4d**, the illumination time on the molecular switch was critical to the logic output such that for the same V_{in} , V_{out} could be different according to the configuration of the molecular switch on surface. In this case, we realized a programmable logic device prototype by modulating the motion state of molecular switch, hence achieving dynamic logic output by UV-Vis illumination. By taking advantage of the azobenzene isomerization, we could define three programmable memory states of the inverter where the molecular switch is at (1) *fully trans* state, (2) *partially cis* state, and (3) *fully cis* state. The logic output results are listed in **Figure 4e** where the molecular switch states programming generates different logic output values for the same input voltage, meanwhile reversible by changing the illumination wavelength. Furthermore, the programmable dynamic logic output could be maintained through input pulse cycles (**Figure 4f**) on long timescale and is reproducible among different devices (**Figure S22**, Supporting Information), hence realizing the logic-in-memory manipulation. More importantly, our fabrication process is less complex and expensive, and features improved tunability thanks to the broadest arsenal of molecular structures switches available.^{4, 53}

CONCLUSION

In summary, we have demonstrated an original and modular concept to exploit on-surface molecular switching events to modulate the electronics of 2D semiconductors. The use of a molecular platform to place light-responsive molecules at a 1 nm distance with a controlled orientation of the molecular dipoles perpendicular to the surface enabled to make full use of the photo-isomerization of azobenzene switches to maximize the reversible doping of 2D semiconductors. Such a dynamic strong doping modulation has a paramount importance for field-effect transistors applications and most importantly also to establish multistate reversible memory current enabled by light stimuli at specific wavelengths. Finally, the integration of molecular switch on logic circuits made it possible to implement light-programmable dynamic logic output simply by tuning the light illumination, thereby realizing an unparalleled prototype of logic-in-memory device. These findings provide unambiguous evidence for the power and versatility of molecular switches when interfaced with 2D materials to accomplish advanced electronic functions, offering a non-conventional solution for the next generation of remotely controlled of (nano)devices.

METHODS

Sample preparation. Monolayer MoS₂, few-layer WSe₂ and graphene were mechanically exfoliated from commercially available crystals (Furuchi, Japan for MoS₂; HQ graphene for WSe₂; Materials Quartz, Inc for HOPG) using the scotch tape method and transferred on thermally oxidized heavily *n*-doped silicon substrates (Fraunhofer Institute IPMS, $\rho_{Si} \sim 0.001 \Omega \cdot \text{cm}$, $t_{ox} = 270 \text{ nm}$). Their thickness was monitored by optical microscope combined with Raman spectroscopy and Atomic Force Microscopy (AFM). The samples were thermally annealed at 200 °C inside a vacuum chamber to

desorb atmospheric adsorbates. CoPc are purchased from Merck. The MX₂/CoPc hybrids were realized by immersing monolayer MoS₂ into 0.5 mM CoPc in DMSO solution for 10 min to attain a high coverage of molecule without degrading the electrical performances of the heterostructure (**Figure S23** in the Supporting information), then rinsed vastly with chloroform, acetone and IPA and thermally annealed in nitrogen to remove aggregates and evaporate solvents. To avoid the desorption of MPC on MX₂ when reacting with ligands in solvent environment, chloroform (which do not dissolve CoPc) was chosen to be the solvent for azopyridinic ligand. The MX₂/MPC heterostructures on Si/SiO₂ substrate were directly immersed into ligand solution at 40 °C for 12h followed by rinsing vastly with chloroform, acetone and IPA and thermal annealing in nitrogen. The functionalized samples are measured after being cooled down to room temperature.

Synthesis of photoswitchable ligand. 4-(4-((4-(trifluoromethyl)phenyl)diazenyl)phenyl)pyridine (TFAP) is synthesized with the following steps. 4-(trifluoromethyl)aniline (400 mg, 2.48 mmol) were dissolved in CH₂Cl₂ (10 ml), a solution of Oxone® (1.525 g, 4.96 mmol) in water (5 ml) was added. The mixture was stirred at room temperature overnight. After that, the organic phase was washed with brine (3 x 25 ml). The solvent was evaporated under vacuum affording 1-nitroso-4-(trifluoromethyl)benzene as a greenish solid that was used without further purification. The crude was then suspended in acetic acid (20 ml) and 4-(pyridin-4-yl)aniline (337 mg, 1.98 mmol) were added and the reaction was stirred at room temperature under inert atmosphere for 24 h. The crude was basified with KOH (6 M) and extracted with ethyl acetate (3 x 25 ml) and the combined organic phases were washed with brine (2 x 50 ml). The solvent was eliminated under vacuum and the product was purified by column chromatography in hexane/ethyl acetate (10/6) obtaining the desired product as an orange powder (350 mg, 53%).

UV-Vis spectroscopy. UV-Vis spectra in solution were recorded on JASCO V-670 spectrophotometer in 1 cm path quartz cuvettes. All the experiments were done using spectroscopic grade solvents. UV and visible light irradiation was done with an optical fiber-coupled LEDs (ThorLabs): for UV light $\lambda_{max} = 367 \text{ nm}$, FWHM = 9 nm, for Vis light $\lambda_{max} = 451 \text{ nm}$, FWHM = 20 nm. UV-Vis spectra on film are measured with CVD-grown monolayer triangle MX₂ film on double-polished sapphire (6carbon, China) without any further transfer process.

UPLC-HRMS measurement. Chromatograms were recorded on an UPLC Ultimate3000 hyphenated to an HRMS (ESI+ Orbitrap) Executive Plus EMR system from Thermo Fisher Scientific. UPLC was run during 3.21 min using a gradient mode, starting with 98% of H₂O (0,05 % formic acid) and 2 % and CAN (0,05% formic acid) with an RP-C18 Hyper Gold Sil from Thermo Fisher at 1.15mL min⁻¹. The quantification of the different isomers was done by integration of all the ionic species generated by each compound. The fraction of the corresponding isomer was calculated as the

area of the isomer divided by the area of the sum of both components and was expressed in %.

Device fabrication. All electronic devices were patterned by photolithography (AZ1505 photoresist and MIF726 developer, Micro Chemicals) using laser writer LW405B from Microtech. For MX₂ MOSFET, 60 nm of gold were thermally evaporated with Plassys MEB 300 following a lift-off process in warm acetone to obtain the final source and drain electrodes. For WSe₂ Schottky junctions, one electrode was first patterned with laser writer and 60 nm Pd was deposited, after lift-off in warm acetone, a second electrode was patterned followed by depositing 60 nm Ag with Egun evaporator Plassys ME300. For MX₂ inverter, the NMOS were first fabricated by patterning the electrode and depositing 60 nm Au. The PMOS were secondly fabricated through the deposition of 60 nm Pd as electrode metal. The devices were rinsed with acetone and 2-propanol to remove resist residues. All devices were annealed under vacuum at 100°C to remove absorbents.

Electrical characterizations. The characterization of device performance was realized by Keithley 2636A and 2635A under N₂ atmosphere. The *in situ* photoswitching is performed by a Polychrome V system (Thermo Fisher) used as monochromatic light source. The output power has been calibrated by a PM100A Power Meter (Thorlabs) where the 365 nm UV light to be 13.5 mW/cm² and 680 nm Vis light to be 15.5 mW/cm². All the electrical measurements were done in dark to exclude the photoconductive effect of 2D materials.

The charge carrier density change Δn upon molecular doping of a semiconducting material, complying with the following equation:

$$\Delta n = \frac{C_{ox} \Delta V_{th}}{e} = \frac{\epsilon_{ox} \Delta V_{th}}{t_{ox} e}$$

where Δn is the change in electron (negative charge) density, C_{ox} is the capacitance per unit area of 270 nm SiO₂, e is the elementary charge, and ϵ_{ox} is the dielectric constant, ΔV_{th} is the change of threshold voltage and t_{ox} is the thickness of dielectric.

Raman and photoluminescence spectroscopy. Raman and photoluminescence spectra were carried out by Renishaw inVia spectrometer equipped with 532 nm laser. The excitation power was kept below 1 mW to avoid local heating damage effects. The wavenumber (energy) resolution was ~ 1 meV.

AFM measurement. AFM imaging was performed by means of a Bruker Dimension Icon set-up operating in air, in tapping mode, by using tip model TESPA-V2 (tip stiffness: $k=42$ N/m).

XPS measurements: CVD-grown monolayer triangle MX₂ film on Si/SiO₂ (6carbon, China) were applied for XPS measurement without any further transfer process. XPS analyses were carried out with a Thermo Scientific K-Alpha X-ray

photoelectron spectrometer with a basic chamber pressure of $\sim 10^{-9}$ mbar and an Al anode as the X-ray source (x-ray radiation of 1486 eV). Spot sizes of 400 μ m and pass energies of 200.00 eV for wide energy scans and 10.00-20.00 eV for scans were used.

Computational details. DFT calculations were performed using the VASP code⁵⁴ using the projector-augmented wave (PAW) basis set. Exchange and correlation effects are treated at the Perdew–Burke–Ernzerhof (PBE) level^{55, 56} with the dispersion forces included by Grimme correction (PBE+D2),²⁻³ with a kinetic energy cut-off of 500 eV and using a Monkhorst-Pack sampling of 2 \times 2 \times 1 for the Brillouin zone (BZ) integration on the unit cell replicated 10 \times 10 \times 1 times with the vacuum spacing set to be 50 Å to avoid the interaction with periodic images. Dipole moment correction was employed along the 'c' axis (Z direction & perpendicular to the TMDC surface). Geometries of MoS₂ and WSe₂ monolayers, as well as the Cis-CoPc(TFAP) and Trans-CoPc(TFAP) adsorbed heterostructures, were fully optimized at the PBE/GGA level of theory prior to the calculation of work function, using a Monkhorst-Pack sampling of 1 \times 1 \times 1 for the Brillouin zone (BZ) integration to minimize the computational cost. The work function (ϕ) of all the systems was calculated as difference of Fermi energy (E_f , taken as the valence band maximum) and the electrostatic potential at vacuum level (E_p).

SUPPORTING INFORMATION

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/XXX>.

Synthetic details, NMR spectra, DFT calculations, optical microscope images, surface characterizations (UV-Vis spectroscopy, AFM, XPS), contrast experiments and statistical analysis of the devices. (PDF)

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Author Contributions

P.S and Y.W. conceived and coordinated the work. Y.W. worked on sample preparation, device fabrication, optical, and electrical characterization. D.I synthesized and characterized the photochemistry of TFAP and CoPc(TFAP). Y.W. and D.I. analyzed the data. S.M.G. did the modelling work, under the supervision of D.B.. Y.W. and P.S. wrote the paper with all the authors contributing to the discussion and preparation of the manuscript.

Notes

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