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Rational Design of Stimuli-Responsive Inorganic 2D Materials via Molecular Engineering: Toward Molecule-Programmable Nanoelectronics

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The ability of electronic devices to act as switches makes digital information processing possible. Succeeding graphene, emerging inorganic 2D materials (i2DMs) have been identified as alternative 2D materials to harbor a variety of active molecular components to move the current silicon-based semiconductor technology forward to a post-Moore era focused on molecule-based information processing components. In this regard, i2DMs benefits are not only for their prominent physiochemical properties (e.g., the existence of bandgap), but also for their high surface-to-volume ratio rich in reactive sites. Nonetheless, since this field is still in an early stage, having knowledge of both i) the different strategies for molecularly functionalizing the current library of i2DMs, and ii) the different types of active molecular components is a sine qua non condition for a rational design of stimuli-responsive i2DMs capable of performing logical operations at the molecular level. Consequently, this Review provides a comprehensive tutorial for covalently anchoring ad hoc molecular components-as active units triggered by different external inputs-onto pivotal i2DMs to assess their role in the expanding field of molecule-programmable nanoelectronics for electrically monitoring bistable molecular switches. Limitations, challenges, and future perspectives of this emerging field which crosses materials chemistry with computation are critically discussed.

1. Introduction

To date, the fabrication of electronics has been mainly monopolized by the conventional Si-based semiconductor processors. The road-map in Si-based electronic devices development has been well defined by a technoeconomic model known as

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Moore's law, postulating that computing power doubles ≈ 18 months, and therefore the dimensions must be reduced by 50% in this above-mentioned duration of time.^[1] Despite their efficiency, the difficulty of downsizing owing to their costly top-down photolithography-based manufacturing principle is approaching their physical limit due to Moore's law. Consequently, a new technological post-Moore era has started with the objective of providing value-added programmable nanoelectronics by implanting new functionalities that do not necessary scale according to Moore's law.^[2-8] In this regard, 2D materials can provide a perfect solution owing to their atomically layered scaling structure and bottom-up functionalization principle, viewing them as perfect building blocks to program the conductive behavior of electronic devices at extreme nanoscale dimensions.^[9,10]

2D materials, as atomically thin layered materials, have been placed in a pioneering position to lead the next "nanoelectronics revolution," which pursues to complement or even replace Si-based semiconductors

in post-Moore electronics.^[5,11–15] Their ultimate thinness in combination with their high surface area plenty of reactive sites represents an excellent atomic structure not only to move electrons, but also to harbor active molecules.[16-18] Indeed, this represents pivotal characteristics to reach novel nanoarchitectures for the development of new forms of computation with ability to process logical binary information at the molecular level. Considering the outstanding results in the field obtained by mainstream graphene (the best known 2D material) and taking into account its absence of energy gap-fact that can hinder the proper implementation of graphene toward logic applications—,^[19-23] the Materials Chemistry community has moved to explore alternative 2D materials exhibiting complementary features, viz., inorganic 2D materials (i2DMs).^[24,25] Amongst the wide family of i2DMs-including grapheneanalogous single-element derivatives (known as Xenes),[26-29] 2D transition-metal chalcogenides (TMCs),^[30-33] 2D transitionmetal carbides/nitrides (MXenes),^[34-37] and 2D transition-metal oxides and hydroxides (TMOs and TMHs, respectively)--,[38-41] semiconductor i2DMs have gained a lot of interest since most ADVANCED SCIENCE NEWS www.advancedsciencenews.com

of their inherent characteristics (e.g., bandgap) can be entirely tuned/modulated by tailoring the nature of the surface substituent via anchoring active molecular components.^[42–45]

In this line, molecular engineering has been positioned as a key eco-friendly technology for the development of functional materials,^[46-52] making it possible the confinement of active molecular components onto passive semiconductor materials by employing sustainable bottom-up synthetic methods. Thus, molecular engineering allows for the design of molecule-based functional materials exhibiting responsiveness to external stimuli, fact that can promote bistable molecular switches through the translation of a nanoscale signal into a readable macroscopic effect.^[53,54] Although extremely motivating from a scientific point of view, a key challenge in the field relies on retaining the bistability of the active molecules exposed on the material's surface of interest. Hence, the convergence of i) the outstanding properties of emerging i2DMs, and ii) the limitless variety of molecules that can be custom-designed and synthesized with predictable functionalities, clearly offers a promising avenue to create stimuliresponsive i2DMs exhibiting programmable behaviors to advance in the field of post-Moore electronics.

In the past five years, a large number of reviews summarizing the preparation, characteristics, and potential applications of 2D materials in general, and i2DMs in particular have been reported.^[15,45,55–83] Nonetheless, a current gap in the field can be clearly identified: the lack of investigation on stimuli-responsive i2DMs for logical information processing at the molecular level. This fact can be mainly ascribed to the necessity of integrating robust covalent immobilization approaches for functionalizing i2DMs with ad hoc active molecular moieties. Consequently, a review including the remarkable merits of covalently engineering stimuli-responsive i2DMs to promote the further development of the expanding field of molecule-programmable nanoelectronics is demanded. In what follows, this Review begins with a brief overview of potential i2DMs to be explored, highlighting their inherent features. Then, different molecular engineering approaches-mainly focused on covalent molecular functionalization methods-to functionalize a la cartè i2DMs with molecular components will be introduced, paving the bases to provide a robust molecular immobilization. Next, prominent examples of stimuli-responsive molecular and supramolecular switches triggered by different external inputs (e.g., optical, electrical, thermal, chemical, etc.) will be presented, since they are the source of inspiration of many logical binary applications. Finally, the promising implementation of stimuli-responsive i2DMs in the field of molecule-programmable nanoelectronics will be discussed, pointing out specific examples of bistable molecular switches. Overall, it is hoped that this Review could provide a comprehensive strategy for the custom molecular modification of i2DMs to expand their integration in the exciting research area of post-Moore devices by implanting the inherent molecular responsiveness of active molecular components on emerging i2DMs.

2. Inorganic 2D Materials

In the past two decades, carbon allotropes made of hexagonal arrangements of sp²-bonded carbon atoms have led the branch of Nanotechnology.^[84–89] After the discovery of fullerene^[90] (0D) and

carbon nanotubes^[91] (1D), the field of 2D materials had a turning point in 2004 after the isolation of graphene from graphite, which was first reported by Novoselov et al.^[23] 2D materials benefit from their thin layered skeleton that provides them with outstanding physicochemical properties different from those of their bulk counterparts. For example, graphene, the most studied 2D material, exhibits excellent electrical, thermal, optical, and mechanical features, amongst other, making it attractive for being used in a vast number of applications.^[92-101] Nonetheless, some applications of graphene in the nanoelectronics field are limited due to the zero bandgap. Indeed, the bandgap is one of the most important parameters in electronic devices, since its presence is imperative to promote interband tunneling for switchability.^[22] Consequently, the field of nanoelectronics demands to explore for alternative semiconductors with similar, but complementary graphene-like layered structure features in order to fill the entire spectrum of electronic properties.

Succeeding graphene, the family of 2D materials-defined as crystalline materials comprised by few atomic layers with strong in-plane interatomic interactions but weak out-of-plane van der Waals forces-has been worldwide broaden in the last decade thanks to their distinct properties (e.g., atomic-level thickness, finite bandgap, absence of dangling bonds, wide flexibility, and high specific surface area plenty of active sites), which are of great importance for new-generation nanoelectronics.[14,102-106] Although more than 100 members have been predicted theoretically, only tens of them have been synthesized experimentally.^[80] Amongst the extensive library of 2D materials, including organic 2D materials,[107-115] inorganic 2D materials (i2DMs, described below), and hybrid organicinorganic 2D materials^[16,116–120] (see Figure 1 for illustration), this Review is specifically focused on the exploration of i2DMs, and therefore both organic 2D materials and hybrid organicinorganic 2D materials are out of the scope. In particular, the family of i2DMs can be basically categorized in four types: 1) 2D elemental analogues of graphene (Xenes),^[121,122] 2) 2D transition-metal chalcogenides,^[123,124] 3) 2D transition-metal carbides/nitrides (MXenes),^[34,125] and 4) 2D transition-metal oxides and hydroxides (TMOs and TMHs).^[40,126] In general, while Xenes are mainly synthesized via top-down chemical approaches (i.e., chemical vapor deposition, CVD), most of the rest i2DMs can be obtained through a bottom-up exfoliation of their bulk counterparts, resulting in 2D materials made of few layers with nanosheet morphology.^[127]

2.1. Elemental Graphene Analogues (Xenes)

Motivated by the possibility of reducing elements beyond carbon into their graphene-like 2D counterparts, a new family of elemental honeycomb-structured 2D materials known as Xenes was born, where X refers to the main group elements ranging from Group IIIA to Group VIA, while the Latin suffix "ene" (meaning sheets) is used to emphasize their layer form as an analogy to graphene.^[121,128] Xenes were initially designed to expand the family of 2D materials belonging to the Group IVA^[129]—viz., silicene (2010),^[130] germanene (2014),^[131] stanene (2015),^[132] and plumbene (2019),^[133]—resulting in the 1st generation of Xenes. To date, the current portfolio of Xenes has







Figure 1. Map of 2D materials formed by 2D organic materials: polymers, covalent-organic frameworks (COFs), organic small molecules (OSMs), and carbon materials (CMs); 2D inorganic materials: elemental analogous of graphene (Xenes), transition-metal chalcogenides (TMCs), transition-metal carbides/nitrides (MXenes), and transition-metal oxides/hydroxides (TMOs/TMHs); and 2D hybrid organic–inorganic materials: metal oxide frameworks (MOFs), hybrid perovskites, and molecular and (supra)molecular hybrids.

been extended to fifteen non-graphene Xenes predicted theoretically, where 13 of them have been also created experimentally, with only indiene^[134] and aluminene^[135] remaining. The ongoing 2nd generation of Xenes, which relates the neighboring elements of the periodic table adjacent to Group IVA, includes: Group IIIA^[136]—borophene (2015),^[137] gallenene (2018),^[138] and thallene (2020),^[139]—Group VA^[140]—phosphorene (2014),^[141] arsenene (2018),^[142] antimonene (2016),^[143] and bismuthene (2017)^[144]—and Group VIA^[145]—selenene (2017)^[146] and tellurene (2014),^[147]—each of them displaying a large number and variety of optical and electronic properties to be exploited for different applications.^[128,148–156] Unlike the ideally planar honeycomb structure of graphene due to the sp² hybridization of carbon atoms, Xenes all prefer alternative anisotropic lattice structures with alternating degrees of out-of-plane atomic buckling (sp²-sp² hybrid) and puckering (sp³).^[150,157] For example, borophene cannot form graphene-like stable honeycomb structure since B only contains three valance electrons (rather than carbon, that contains four), while phosphorene-the lightest stable elemental Group-VA Xene-can form five different allotropic forms, including orthorhombic (black phosphorene) and bucked honeycomb (blue phosphorene) structures.^[158] Thus, the physicochemical properties of Xenes are not only ascribed to the na-

ture of the element but also associated with its specific atomic arrangement.^[60,150,159] **Figure 2** illustrates an historical view of the two generations of Xenes with its corresponding most stable atomic structures.

2.2. Transition-Metal Chalcogenides

Chalcogenides—also known as "ore formers,"^[160] coming from the Greek words "chalcos" (ore) and "gen" (formation)—are defined as a group of inorganic materials and compounds containing elements of the Group VIA of the periodic table, including sulfur, selenium, and tellurium, but excluding oxygen (since oxides have very different chemical behaviors) and polonium (because its radioactivity).^[161] Thus, TMCs are related to those i2DMs consisting of at least one chalcogen anion (S^{2–}, Se^{2–}, and/or Te^{2–}) and at least one metal cation (which include some 3d–5d early transition metal elements). TMCs are usually classified with regarding to their number of chalcogen ions (e.g., mono-, di- or tri-chalcogenides), being 2D transitionmetal dichalcogenides (TMDs) as MX_2 —where M is a transition metal atom (e.g., Mo, Ti, W, V or Nb) and X is a chalcogenide atom—the most studied, and therefore explored ones.^[31,32,162,163]



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Figure 2. A) Periodic table highlighting the synthesized single-element 2D materials (graphene and Xenes) from Group IIIA to Group VIA with its corresponding year of publication. B) Most stable graphene-like atomic structures of Xenes (balls correspond to atoms and lines represent interatomic bonds), also presenting the typical flat honeycomb lattice of graphene (C, Group IVA) for comparison. Adapted with permission.^[150] Copyright 2020, Elsevier.

Particular attention has been paid to TMDs due to their unique combination of atomic-scale thickness, direct bandgap, and favorable mechanical and electronic features,^[164,165] representing an alternative group of 2D materials that compensates, for example, the intrinsic semimetallic nature of graphene or the insulating characteristics of hexagonal boron nitride^[166] (h-BN). In this regard, the inherent characteristics of TMDs are strongly influenced by their composition nature, spanning the entire range of electronic structures from semiconductors (e.g., $MoS_2^{[167]}$ $WS_2^{[168]}$) to semimetals (e.g., WTe_2 ,^[169] TiSe₂^[170]), true metals (e.g., $NbS_2^{[171]}$) or superconductors (e.g., $TaS_2^{[172]}$). In general, the link between TMDs relies on the van der Waals interactions between different covalently sandwiched X-M-X monolayers (two chalcogenide planes separated by a transition metal plane) that stacked the bulk 3D crystals-in parallel to the stacked layers of graphene forming the bulk graphite—, where M can have either octahedral or trigonal prismatic coordination (see Figure 3 for illustration). In addition, TMDs can adopt different phases or polymorphs, where the preferred one depends upon the d-electron count of the transition metal, which is, indeed, a predominant factor in determining its electrical and conductive properties.^[32,173,174] For example, just the MoS₂ can exhibit five different polytypes, such as 1H, 2H, 3R, 1T, and 1T', [32] where the letter initial integer indicates the number of layers in the unit cell, while the letter corresponds to the type of symmetry (H, R, and T represent hexagonal, rhombohedral, and tetragonal symmetry, respectively). Thus, the inherent physicochemical characteristics of TMDs with regarding the crystal structure, in combi-

nation with their less covalent nature and low electronegativity, make them excellent candidates for their implementation in a wide range of nanoelectronics applications.^[30,175–181]

2.3. Transition-Metal Carbides/Nitrides (MXenes)

The family of the so-called MXenes^[184–186]—with a general chemical formula: $M_{n+1}X_nT_x$, where M is an early transition metal, X is either C and/or N, and T, refers to the surface-terminating functionality (commonly: -O, -OH, and -F groups)-was first introduced by Gogotsi and co-workers in 2011.^[187] Analogously to the procedure to obtain layered graphene from bulky graphite, they demonstrated the suitability of selectively etching the Agroup out of 3D bulk ternary transition metal carbides/nitridesknown as MAX phases,^[188] being A mostly an element of Group IIIA and IVA-by using a fluoride-based chemical (i.e., hydrofluoric acid, HF) as an exfoliating agent (see Figure 4 for exemplification). Since then, this family of i2DMs has growth rapidly, with a current library longer than thirty members experimentally synthesized successfully (e.g., $\text{Ti}_3\text{C}_2,^{[189]}\text{Ti}_2\text{C},^{[190]}$ V_2C ,^[191] Cr_3C_2 ,^[192] Nb_4C_3 ,^[193] Fe_2C ,^[194] Mo_2C ,^[195] Hf_3C_2 ,^[196] Ta_2C ,^[197] Cr_2N ,^[198] Ti_4N_3 ,^[199] etc.), and dozens more studied theoretically.^[200]

The structure of MXenes is based on hexagonal close-packed layers of M and X, interleaved one with other, while T_x active groups are randomly distributed on the surface. In this regard, T_x active groups play a pivotal role in determining the



Figure 3. A) Early transition metal (M) and chalcogen (X) elements from the periodic table forming TMD crystals. B) Metal coordination and common stacking sequences for 1:2 (X–M–X) TMD: H phase (1H, 2H, and 3R) and T phase (1T and 1T'), showing the crystal structure from both top and side views. Adapted with permission.^[182] Copyright 2020, Annual Reviews. C) HRTEM image of few layers of MoS_2 as a model TMD. Reproduced with permission.^[183] Copyright 2016, Elsevier.

material properties of MXenes.^[203–210] Nowadays, titanium carbide (Ti₃C₂T_x) is one of the most widely MXene studied thanks to its unique set of properties, including high electrical conductivity and mechanical features, high negative zeta-potential, biocompatibility, large area-to-volume ratio, good chemical stability, tunable surface functionality, and efficient absorption of electromagnetic waves.^[34] Such a combination of properties, together with the inherent metallic conductivity determined by their free electrons as well as hydrophilicity caused by surface terminations, makes MXenes as excellent candidates for a large number of nanoelectronic applications.^[185,211–214] In this last regard, the term MXetronics has emerged to allude to the electronic and photonic applications of MXene-based devices.^[211,215–217]

2.4. Transition-Metal Oxides/Hydroxides

TMOs and TMHs constitute an important class of i2DMs owing to their unique layered structures and variable chemical compositions, being possible to be used for a wide range of nanoelectronics, optoelectronics, and/or photonics applications.^[39,218–222] Both of them can be classified into two main families: i) binary and ternary 2D TMOs, referring to those oxides containing either one or two metal elements in the formula, respectively,^[223] and ii) single and double 2D TMHs, referring to those hydroxides containing a metal with either a single oxidation state or a mix of oxidation states, respectively.^[224] In general, there are two major strategies to synthesize both 2D TMOs and 2D TMHs: top-down and bottom-up methods, being the top-down chemical exfoliation approach the easiest and fastest way for isolating layered oxides/hydroxides from the parent bulky precursor.^[225–227] The extensive variety of different TMOs/TMHs crystal structures is the result not only of the diverse stable valance states of the transition metal constituents, but also of the various crystal phases that some of them present (see **Figure 5**).

On the one hand, TMOs are a class of semiconductors that despite being mainly camouflaged by TMCs (probably because TMOs exhibit, in general, wider bandgap energies),^[228] they present a series of benefits, including not only good electron transport properties that alleviate the fast charge





Figure 4. A) Elements in MAX phases and MXenes. Reproduced with permission.^[201] Copyright 2021, Springer. B) Typical synthesis and delamination of MXene from MAX phase via selective etching with its corresponding atomic structures (exemplification of an M_3AX_2 phase transformation (e.g., Ti_3AlC_2) into $M_3X_2T_x$ (e.g., $Ti_3C_2T_x$). Table of colors: M: blue, A: red, X: purple, T: gray. C) SEM images representing i) Ti_3AlC_2 phase, ii) Ti_3C_2 MXene, and iii) delaminated $Ti_3C_2T_x$ (MXene. Reproduced with permission.^[202] Copyright 2017, Elsevier.

recombination characteristic, but also lower synthetic costs and higher chemical stability in air when compared to that of TMCs.^[229,230] For example, in nature exists a vast variety of layered TMOs-composed of stacked, negatively charged slabs with surrounding alkali metal cations occupying the interlayer space-that have been successfully delaminated, as the case of $K_{0.8} Ti_{1.2} Fe_{0.8} O_4, \ KCa_2 Nb_3 O_{10} \ \text{or} \ Cs_{6+x} W_{11} O_{36}.^{[38]}$ The most representative example of TMO is TiO₂, but the atomistic structures of the majority of studied 2D TiO₂ materials remain still unclear, in which anatase seems to be the most common crystal structure in the 2D configuration.^[231,232] Nonetheless, the wide optical bandgaps of TiO₂ (3.2–3.4 eV) restrict the light absorption only in the ultraviolet region.^[233] Thus, the research of 2D TMOs has been mainly focused on exploring binary TMOs with bandgap energies in the range of 2.6–3.0 eV to lie in the visible light region, as the case of MoO_3 , ^[234] WO_3 , ^[235] Ga_2O_3 , ^[236] and V_2O_5 . ^[237]

On the other hand, TMHs are regarded as a novel family of functional i2DMs with outstanding performances as electrocatalysts and energy systems. The general crystal structures of 2D TMHs are brucite-type single or hydrotalcite-type double 2D TMHs.^[226] Both of them are built of octahedral units (slabs) of brucite-like layers linked by edges, which are constituted by six OH⁻ groups placed in the corners of the octahedron, while a divalent and/or trivalent metal cation is positioned in the center. In the case of hydrotalcite structures in double 2D TMHs,—with a general formula: {[$(M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A_{x/n}]^{n-}\cdot mH_2O$ }, where M^{2+} and M^{3+} is a divalent and trivalent metal cation, respectively, and A^{n-} is a charge-balancing interlayer anion—, those brucite-like layers are intercalated one with other through water molecules and organic/inorganic anions, forming van der Waals and electrostatic interactions with the hydroxyl groups of the host layers.^[238]

3. Molecular Engineering of i2DMs

Molecular engineering is becoming a powerful tool in the field of 2D materials to fulfill the central challenge of materials science: the design of materials with programmable functions.^[17] The assembly of active molecular components (i.e., stimuli-responsive molecules) supposes an excellent opportunity to enrich the functionalities and complement the limitations of i2DMs according to task-specific applications. The fact of selecting and adapting the active molecular constituent anchored upon the substrate not only provides a custom way to modulate and/or manipulate most of the physicochemical features of pristine i2DMs (e.g., optical, electronic, and thermal properties), but also helps to control the interactions between the material and its surrounding environment. In particular, molecular functionalization can have a

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Figure 5. A) Representative structures of selected single TMO nanosheets whose bulk counterparts are naturally layered. Reproduced with permission.^[38] Copyright 2018, Elsevier. B) Basic structure of a double 2D TMH polytype, showing how the interlayer anions and water molecules intercalates the octahedral units of brucite-like layers in a hydrotalcite structure.

profound effect on the optical and electrical properties of i2DMs. From an optical point of view, one of the most significant effects of molecularly functionalizing i2DMs is the modulation of their bandgap, leading to changes in their absorption spectra by introducing new electronic states within the band structure.^[239] Otherwise, the electrical conductivity of i2DMs can also be modulated through molecular engineering, for example, by promoting changes in carrier mobility, shifts in the Fermi level, and even doping effects (i.e., n-type or p-type doping) via charge transfer between the i2DM and the anchored molecule.^[240] Thus, by implanting foreign active units, further possibilities are enabled to cover the current gap in i2DMs due to the acquisition of programmable molecular features.^[241]

Besides the impressive inherent features demonstrated by the aforementioned families of i2DMs, a main bottleneck that hinders the proper implementation of i2DMs in the field of nanoelectronics can be clearly identified: the lack of sound functionalization strategies to anchor ad hoc active (supra)molecular components upon i2DM substrates for tuning their (opto)electronic properties.^[242,243] The controlled preparation of robust molecule-rich i2DMs might provide a valuable path to reach stimuli-responsive i2DMs performing reproducible and quality electrical characteristics, a must toward the development of complementary-logic devices and circuits. Indeed, the benefit of integrating stimuli-responsive molecules as active building blocks upon i2DMs is that programmable nanoelectronics can be reached, since the electronic properties can be modulated reversibly.

In general, two main categories arise when thinking about the different ways of interfacing i2DMs with active molecular components, which relate to noncovalent^[244] and covalent functionalization methods^[245,246] (vide infra). Both meth-

ods utilize molecular components as building blocks to tune the physicochemical features of i2DMs, while the nature of interactions—nonbonded or bonded ones—will depend on the chemistry of the selected i2DM with the reactive groups from the ligand.^[247]

3.1. Noncovalent Molecular Functionalization of i2DMs

Noncovalent functionalization approaches rely on nonbonding interactions between the selected i2DM with the molecular component via weak physical adsorption, being the stabilization forces involved strong enough to overcome entropic factors driving disassembly. The major noncovalent phenomena in i2DM molecular functionalization are usually manifested as i) van der Waals interactions (referring to weak distance-dependent nonionic forces),^[248] ii) dipolar interactions (involving electrostatic forces),^[249] iii) charge transfer interactions (occurring across electron donor-electron acceptor systems),^[250] and iv) H-bond interactions^[251] (an special type of dipolar interaction that takes place between neighboring H atoms and a highly electronegative atom, such as N, O, or F). Briefly, noncovalent molecular approaches have the advantage of retaining the crystal structure of i2DMs unaltered, fact that preserves the (opto)electronic properties of the pristine material.^[17] Nonetheless, such weak interactions usually lead to molecule desorption during the taskspecific application, a fundamental drawback that hinders its proper implementation toward the monitoring of bistable molecular switches. Following the scope of this Review and considering that a strong molecule-material interaction is a must to provide efficient molecular switches, noncovalent molecular approaches have been excluded of revision.

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3.2. Covalent Molecular Functionalization of i2DMs

Covalent molecular approaches relate to the formation of a chemical bond between the ligand identity (i.e., active molecular components) and the skeleton of i2DMs.^[252] Such chemical bonding can occur either directly into the i2DM sheets or indirectly through the functional groups exposed on the surface of some i2DMs. In general, the covalent functionalization of i2DMs via wet-chemical approaches allows for molecularly binding on both sides of the plane.^[253] The main benefits of anchoring molecules to i2DMs via strong bonding interactions are: i) enhanced stability (the covalent bond ensures that the molecular component will remain anchored to the i2DM during device operation, preventing molecular desorption), ii) control over molecular orientation (crucial to understand the mechanism behind the molecular switch), iii) longterm durability (longer operational lifetime is expected owing to the strong and stable covalent bond), iv) reduced moleculemolecule interactions (preventing undesirable interference signals and therefore, enhancing device performance), and v) largescale manufacturing (covalent molecular functionalization can be adjusted to mass production, simplifying the manufacturing of molecule-programmable nanoelectronics with reproducible electronic performances). However, since covalent bonds are irreversible and permanently modify the material surface, the perfect structure of i2DMs can be significantly affected, and therefore the electronic and structural characteristics of i2DMs can be disrupted.[254]

What follows briefly addresses the main types of covalent interactions that may be promoted when exposing i2DMs to small organic molecular components with regarding the nature of the selected i2DM.

3.2.1. Covalent Functionalization of Xenes

The lack of stability of Group IV-Xenes (viz., germanene, silicene, and stanene) under ambient conditions makes them as ideal 2D systems to understand the pivotal role of surface functionalization, since the inclusion of a ligand termination on each atom is a must to reach stable i2DMs.^[255–257] This has resulted in a subclass of Xene-based derivatives known as Xanes (e.g., silicane, germanane, and stanane), where the suffix "-ene" is replaced by"ane" to point out the inclusion of ligand-terminated groups via single bonds ending, analogously to graphane.^[258]

In general, Xanes are obtained by a specific type of direct solidstate chemical approach known as topochemical reaction, which transpires under the strict control of molecular packing in the crystal lattice.^[259] This approach is based on the topotactic transformation of bulkier Zintl phases—the intermetallic-layered precursor made of M₂X, being M an alkaline earth metal (i.e., Ca or Ba) and X the Group IV element—into covalently terminated XR–Xanes (viz., SiR, GeR, and SnR) upon the reaction with either halogen acids or haloalkanes in aqueous media, where the terminal R ligand (R = -H or alkyl group, such as $-CH_3$, CH_2OCH_3 , and $-CH_2CH=CH_2$, respectively) covalently bonds each p-block X atom.^[255] **Figure 6**A exemplifies the general topochemical deintercalation mechanism to transform bulkier Zintl phases into molecule-rich Xene crystals.

Amongst the different family of Xanes, germanane derivatives are the most explored one.^[261-263] By following the aforementioned methodology, Jiang et al. established the role of tailoring the ligand group anchored to germanane (with regarding its size and electronegativity) on modulating the electronic structure of Xanes (Figure 6B).^[260] Indeed, the fact that the bandgap of germanene can be easily tuned by the tethered ligand has increased the interested in developing alternative functionalization methods to widen the library of 2D-GeR derivatives in order to advance toward the development of versatile and robust synthetic methods capable of customizing Xanes with the desired molecular component; for example, by the inclusion of Grignard reactions on previously synthesized 2D-GeI (Figure 6C),^[264] or by *click*ing thiol-rich molecular components upon 2D-GeCH₂CH=CH₂ via a thiol-ene click reaction (Figure 6D).^[18,120] In this last regard, Muñoz et al. also exploited this *click* approach to reach organic-inorganic 2D-germanene heterostructures by covalently anchoring thiol-rich carbon dots.^[120] Further germanene functionalization approaches have been recently summarized by Ng and Pumera^[265] and Hartman et al.^[266] Regarding to the family of silicanes, the so-called siloxene— $[SiH_{1-x}(OH)_x]$, whose structure is terminated with -H and -OH ligands-is probably the most exploited one.^[267] Beyond the general topotactic transformation of Ca₂Si with halide acids, a direct chemical synthesis of benzyl-modified silicane has been successfully achieved from bulky Ca2Si.^[268] Comparing to silicane and germanane derivatives, the synthesis of stanane derivatives (SnR) is almost an unexplored field, fact that can be ascribed to the propensity for oxidation of its crystalline Zintl phase precursor (BaSn₂).^[269,270]

Regarding to alternative Xenes, Group-V Xenes, such as phosphorene and arsenene have been successfully covalently functionalized with different molecular moieties by different chemical methods. On the one hand, the chemistry of black phosphorus offers two main covalent functionalization routes, as shown in Figure 7: the direct formation of P-C bonds via either diazonium salts^[271] (Figure 7A) or nucleophilic attack of P groups,^[272] and the indirect formation of P-O-C bonds by taking advantage of the reactivity of the -OH groups present on its surface (owing to its oxidation with air) with nucleophilic reagents.^[273] Alternatively, the use of aryliodonium salts has shown to provide both P-C and P-O-C bonds, resulting in a greater covalent functionalization (Figure 7B).^[274] On the other hand, the chemistry of gray arsenic has been mainly limited to the reactivity through the nonbonding electron pairs of As, which allows coordination with organometallic compounds (e.g., [Cr(CO)₆] via UV irradiation),^[275] as well as As=C bond formation with reactive carbene-based species (Figure 7C).^[276]

3.2.2. Covalent Functionalization of TMCs

The covalent molecular functionalization of TMCs in general, and TMDs in particular, can be mainly summarized in four chemical approaches (see **Figure 8**): i) thiol-based molecular chemisorption via vacancy engineering,^[277–279] ii) direct S–C bond formation using reactive diazonium salts,^[280] iii) thiol–Michael *click* addition,^[281] and iv) nucleophilic reactivity through phase transition engineering,^[246] where the proper functionalization strategy is highly influenced by the crystal phase of



Figure 6. A) Schematic of the topochemical deintercalation of Zintl phases, such as Ca_2Ge or Ca_2Si , with R halides (R = H or alkyl chains) to reach silanene and germanane derivatives (Xanes). B) E_2 Raman shifts in ten different GeR derivatives plotted as a function of their absorption onsets (bandgaps). Reproduced with permission.^[260] Copyright 2016, American Chemical Society. Alternative functionalization of previously synthesized C) 2D-Gel via Grignard method, and D) 2D-GeCH₂CH=CH₂ via thiol–ene *click* chemistry.

the pristine TMD. What follows describes the different chemical approaches to covalently tether a wide variety of molecular components onto TMDs, using MoS_2 as a model TMD; however, these methods can be simply extended to additional TMDs (e.g., WS_2 and $MoSe_2$).

First, vacancy engineering is probably the most exploited approach for covalently tethering small molecules onto the surface of 2H-MoS₂. Briefly, the 2H phase is the most thermodynamically stable form of MoS₂, which exhibits a semiconducting nature but an almost inner reactivity. Thus, a simple way to modify 2H-MoS₂ is by taking advantage of its naturally occurring sulfur vacancies (SV) in its lattice during chemical exfoliation, where thiol-rich molecules can spontaneously occupy those defects by following the reaction: $[R'-SH + SV-MoS_2 \rightarrow$ R'-S@MoS₂(H)] (Figure 8A).^[282,283] Importantly, this particular functionalization approach well preserves the physical structure of the resulting molecule-rich TMD. Nonetheless, some computational works cast doubt on the resultant products and reaction mechanisms, demonstrating that other subproducts via repairing pathway ($[R'-SH + SV-MoS_2 \rightarrow MoS_2 + R'-H]$) and dimerization pathway ($[2R'-SH + SV-MoS_2 \rightarrow (R'-S)_2 + MoS_2(H-H)]$) can also be considered.^[284] Beyond thiol-rich molecules, Canton-Vitoria et al. also demonstrated the suitability of covalently anchoring 1,2-dithiolenes on MoS2 nanosheets.^[285] As validated by density functional theoretical studies and material characterization experiments, this functionalization occurs by taking advantage of the high binding affinity of 1,2-dithiolenes toward Svacancy-based Mo atoms, particularly those located at the edges of the i2DM. Overall, vacancy engineering is a facile molecular functionalization strategy, which offers the advantage of keeping intact the basal plane of MoS₂, while preserving their semiconducting character.

Second, an additional approach for covalently anchoring organic molecules on unmodified 2H-MoS₂ is through a radicalmediated reaction utilizing diazonium salts, where a robust S-C bond can be formed triggered by the presence of S-vacancies that serve as nucleation centers for the initial functionalization (Figure 8B).^[286] The mechanism proposed follows three sequential steps: 1) rapprochement of the diazonium salt derivative (R'- $Ar-N_2^+$) upon the i2DM surface, where 2) a surface charge rearrangement allows the N₂ group to break off, forming a radical group (R•) that promotes 3) a covalent C-S bond formation. This strategy has shown to be very useful for molecularly engineering not only different TMCs (e.g., MoS₂, WS₂, MoSe₂, and WSe₂), but also alternative TMDs, such as Bi₂S₃ and Sb₂S₃.^[287] For example, Miller et al. demonstrated the suitability of modulating the work function of MoS₂ by tailoring the terminal R' group of the covalently grafted aryldiazonium salt, resulting in a reduction or increase of the work function when employing electron-donating or electron-withdrawing R' groups, respectively.[288]

Third, the thiol–Michael addition reaction—included into the *click* chemistry toolbo^[289]—has also been successfully exploited

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Figure 7. Proposed mechanisms for the covalent molecular functionalization of Group-V Xenes, such as i) black phosphorous via A) direct P—C bond formation (exemplification using diazonium salts) and B) indirect P—O—C bond formation (exemplification employing an iodine-based nucleophilic reagent), and ii) gray arsenic via C) chlorocarbene-mediated As=C bond formation.

for anchoring maleimide derivatives onto 2H-MoS₂ (Figure 8C). In this case, the soft nucleophilicity of S atoms allows the *click* integration of the molecular components through a Michael addition under very mild conditions.^[281] This method has been particularly appealing for the Pérez's group, since further *click* chemistry approaches have been explored, for example, for either the covalent cross-linking of different flakes of 2H-MoS₂ through bismaleimide reagent,^[290] the linkage of graphene to reach 2D/2D heterostructures,^[291] or the formation of succinimide polymer adlayers covalently connected to 2H-MoS₂ by adding a basic reagent (rather than the molecular monolayer of maleimide *clicked* in absence of base).^[292]

Lastly, a fashionable way to overcome the inherent inner reactivity of 2H-TMD—mainly attributed to its neutral charge state that difficult electron transfer—is by employing the so-called phase transition engineering approach.^[246,293] This method relies on converting the semiconducting 2H phase onto the metallic 1T one using *n*-butyllithium, in which its intercalation promotes a partial conversion of the crystal structure via electron transfer, resulting in a negatively charge 1T-TMD nucleophile-like structure allowing the integration of electrophiles, such as alkyl halides and aryldiazonium salts (Figure 8D). Recently, Chen et al. have reported a synthetic strategy for the simultaneous bisfunctionalization of MoS₂ sheets employing both organohalides and diazonium salts.^[294] In addition, phase engineering was also exploited for covalently synthesizing a modified 1T-MoS₂ with terminal phenylazido pendant arms, which was further post-treated with terminal acetylene derivatives via copper-mediated azide–alkyne cycloaddition, a *click* chemistry alternative to further wide the library of molecule-rich TMDs.^[295]

3.2.3. Covalent Functionalization of MXenes

Contrary to Xenes and TMCs, the covalent functionalization approaches for anchoring ligands upon MXenes is mainly focused on exploiting the reactive groups (T_{x}) exposed on its surface,^[296,297] which will also depend on the type and fraction of T_x during production.^[298] Such particularity endows MXenes with negative charged characteristic and high surface activity, opening up a wide range of chemical strategies for molecularly engineering MXenes with ad hoc molecular components. Taking into account that the main reactive groups exposed on MXenes are both halogens and oxygenated groups,^[299] the former $(T_r = halogen groups)$ allows for noncovalent modification approaches (i.e., H-bonds^[300] and electrostatic assembly^[301]), while the latter (T_x = oxygenated groups) makes also possible the implementation of covalent methods.^[297,302] Consequently, exploiting the high reactivity of the different oxygenated groups (e.g., -O-, -OH) is the most primary and direct approach for covalently functionalizing MXenes. On the one hand, the presence of oxygenated groups allows to implement chemical methods similar to the ones carried out on 2D graphene derivatives (i.e., reduced graphene oxide).^[303-305] On the other hand, the fact that the transition metal core is directly connected to T_x makes it possible to see MXenes as MO₂-like structures, and therefore the chemistry to carry out will be close to the one for functionalizing TMOs (ut infra). Consequently, four main covalent molecular approaches for functionalizing MXenes can be considered: i) selfassembling of silanes via Ti-O-Si bond formation,[306] ii) selfassembling of phosphonates via Ti–O–P bond formation,^[307] iii) nucleophilic substitution via Ti-O-C bond formation,^[217] and iv) diazonium salts grafting via radical-induced Ti-O-C bond formation.^[308] Figure 9 summarizes these four main covalent strategies, using $Ti_3C_2T_x$ as a model MXene material.

Self-assembling has shown to be a versatile strategy for covalently anchoring a wide range of molecular components via either silvlation^[306] (Si(OR)₃-R') or phosphorylationf^[307]l $(PO(OR)_2 - R')$ process, where OR corresponds to hydrolysable groups and R' stands for an aliphatic chain carrying a terminal functional group. As shown in Figure 9A,B, the driving force of these two chemical approaches relies on a spontaneous condensation dehydration between the -OH groups from MXene and the OR hydrolysable groups (R = H or alkyl groups) from the coupling agents via esterification/etherification process,^[309] leading to the formation of a new chemical bond (i.e., Ti-O-Si or Ti-O-P). In addition to the resulting chemical bond formation, further noncovalent interactions like H-bond interactions can also be promoted.[310] This method is simple and makes it possible the inclusion of different R' terminal groups. For example, Bagheri et al. demonstrated the suitability of reacting $Ti_3C_2T_x$ MXene with a mix of two different types of silanes, such as (3-aminopropyl)



Figure 8. Proposed mechanisms for the covalent molecular functionalization of TMDs (e.g., MoS₂ and WS₂) via A) vacancy engineering, B) direct S–C bond formation with reactive diazonium salts, C) thiol–Michael *click* addition, and D) phase transition engineering.

triethosysilane and (3-mercaptopropyl) trimethosysilane, for the inclusion of more than one chemical group (i.e., amine and thiol groups^[311]) during the same procedure. This is especially appealing since the R' terminal groups can be utilized for further functionalization.^[312]

Beyond silvlation and phosphorylation, other type of organic molecules (e.g., catechols,^[313] carboxylic acids,^[275] or isocyanate groups^[314]) can be anchored on Ti₃C₂T_x–MXene via nucleophilic substitution, resulting in a new Ti-O-C bond formation. On the one hand, carboxylic acids and catechols are grafted on MXenes through an esterification process (catalyzed by protons) followed by a dehydration reaction.^[315] In general, the functional reactive groups of the selected molecular components are previously protonated in acidic media solution (e.g., $-C-OH_2^+$, $-C=OH^+$), resulting in an electrophilic carbon that can be attacked by the nucleophilic MXene rich in surfaceterminating -OH groups, with subsequent removal of H₂O (Figure 9C).^[217,316] On the other hand, a carbamation process occurs when MXene is exposed to isocyanate groups in presence of a tertiary amine, which plays a fundamental role to catalyze this reaction.[317]

Otherwise, diazonium salts derivatives (e.g., aryldiazonium salts) have also demonstrated its suitability not only for providing covalently bonded TMCs, but also MXenes (Figure 9D).^[313] In general, this strategy relies on in situ forming the diazonium salt derivative by reacting a primary amine with nitrous acid. Afterward, the resulting diazonium salt releases N₂ (g) derived from the acquisition of an electron from the MXene surface, inducing the formation of a reactive free carbon radical that gives rise to a new Ti–O–C bond. Briefly, the highly negative Zeta potential of MXenes provides them with free electron clouds that guarantee the grafting of diazonium salts.^[318]

Finally, it is important to highlight that less-frequently molecular covalent functionalization on MXenes have also been reported, as the case of 1) the direct Ti—N bond formation on $Ti_3C_2T_x$ –MXene with glycine^[319] or 2) the direct in situ formation of metal nanoparticles (M-NPs, such as Ag-NPs and Au-NPs) on $Ti_3C_2T_x$ –MXene using a metal ion precursor (M^{*n*+}),^[320] which they are used as nanotemplates for the incorporation of thiol-rich molecules via M—S bond formation.^[321]

3.2.4. Covalent Functionalization of TMOs/TMHs

As mentioned above, the chemistry of TMOs will be very similar to the one utilized for MXenes owing to their MO₂-like structure. In general, metal oxides react with air, forming surface-bonding hydroxyl groups that favor reactivity with a wide variety of reactive groups in solution,^[322] including silanes,^[323] phosphonates,^[324] carboxylic acids,^[325] diazonium salts,^[326] catechols,^[327] alkynes/alkenes^[328] or thiols,^[329] as depicted in **Figure 10**. In parallel, same approach can be thought when using TMHs, since their —OH groups play a pivotal role in surface modification.^[330] Nonetheless, taking into account that the implementation of both 2D TMOs and 2D TMHs is still in an early stage, their covalent functionalization with molecular components is almost an unexplored field, and therefore there is still plenty of room to explore.^[331]



Figure 9. Proposed mechanisms for the covalent molecular functionalization of MXenes (e.g., $Ti_3C_2T_x$ –MXene, being $T_x = -OH$ groups via A) silylation, resulting in a Ti–O–Si bond formation, B) phosphorylation, with the corresponding Ti–O–P bonding, C) nucleophilic substitution, resulting in a new Ti–O–C chemical bond, and D) radical-induced Ti–O–C bond formation using diazonium salts derivatives.

The covalent functionalization of TMOs/TMHs using silanes $(Si(OR)_3 - R')$ and phosphonates $(PO(OR)_2 - R')$ coupling agents through self-assembling is probably the most explored route for anchoring molecular moieties, since it allows for a rapid and spontaneous formation of a robust molecule-TMO/TMH linkage,[332] resulting in a new chemical bond (i.e., M-O-Si or M-O-P). In addition, the reactive R' group can be further utilized for additional chemical modifications. For transition metal oxides like TiO₂ and ZrO₂, phosphonates have proven to be more stable than silanes in the pH range of 1–10.^[333] Moreover, Zeininger et al. provided a toolbox to identify optimal monolayersurface combinations on TiO₂ surfaces exploring different bindings with phosphorous, carboxylic acids, and catechol ligands, demonstrating that phosphonic acids were preferable compared to catechols and carboxylic acids.^[334] Additionally, alternative covalent approaches have been reported for 2D TMOs. For example, Zhong et al. covalently interfaced 2D TiO2-TMO with oxidized graphitic C₃N₄ molecules via Ti–O–N binding.^[335] Although experimental characterization did not really evidence the covalent nature of the anchoring, DFT calculations clearly demonstrated the feasibility of the chemical bond. Additionally, Atanasova et al. reported the direct M—S bond formation on ZnO–TMO using azide-functionalized thiol linker molecules.^[336] Regarding to 2D TMHs, Dou et al. covalently anchored a catecholate ligand (i.e., dopamine) upon 2D Mg/Al-TMH—which was subsequently modified with a copolymer (i.e., poly(methyl vinyl ether*alt*-maleic anhydride) by conjugating the anhydride groups of the copolymer to the amine groups of dopamine—for the preparation of a mussel-inspired layered double hydroxide material for the removal of copper ions.^[337]

4. Stimuli-Responsive Molecules Triggered by Different External Inputs

In recent years, the materials science community has evolved from passive to active materials.^[53,338–341] While the properties of passive materials cannot be modified postsynthesis, those of active materials can be modulated by simply applying an external stimulus. In general, external stimuli can be of i) physical (e.g., light, electrical bias, temperature, ultrasounds, force,







Figure 10. Main covalent molecular approaches for functionalizing TMOs and TMHs with molecular components by taking advantage of the -OH groups exposed on the i2DMs' surface.

magnetic field, etc.) or ii) chemical (e.g., pH, ions, supramolecular host-guest interactions, biochemical agent, redox species, etc.) origin.[342-345] In this regard, molecular engineering has allowed the development of responsive materials, which result from the confinement of active molecular and supramolecular components upon materials that act as bistable switches.^[346] Active molecules can respond to changes in their environment; consequently, the translation of a molecular change-triggered by an external input—into a readable output signal can be achieved. Bistability refers to the existence of two or more thermodynamically (meta)stable states in a single system, capable of being reversibly interconverted between them in response to an external stimulus.^[347] This fact influences the system depending on the state, and therefore allows the possibility of reading out the system as binary logic data (0, 1). Thus, molecularly engineering of stimuli-responsive materials by implanting the inherent active characteristics of active molecules represents an efficient pathway toward processing binary logic operations at the molecular level.

Active molecules responding to externally applied physical or chemical stimuli, have shown to be very promising for developing a wide variety of stimuli-responsive materials acting in a controllable and predictable fashion (programmable properties), such as polymers,^[348–352] nanocarriers,^[353–358] 2D materials,^[359–364] supramolecular macrocycles,^[365–368] micro-/nanomotors,^[347,369,370] 3D printed platforms^[54,371–375] or solid substrates,^[376–379] amongst other. The selection of a stimulus will depend on the characteristic of the molecular component (sensitivity to a specific type of stimuli), its capability to promote a particular change on the anchored material, and the specific task application.^[380] Some of the advantages of implanting molecular switches on materials/surfaces relies on i) high precision design at the molecular level, ii) low energy operando, iii) rapid response time, and iv) tunability and reversibility of the optoelectronic properties. However, it can also involve some drawbacks, such as i) limited operating conditions, ii) short-term stability (durability), iii) costly large-scale production (scalability), and iv) versatility for different applications.

What follows summarizes prominent examples of molecular components displaying bistable active forms in solution when they are subjected to different external triggers, a key aspect to consider when engineering stimuli-responsive materials in general, and stimuli-responsive i2DMs in particular.

4.1. Molecular Switches Triggered by Physical Inputs

Physical stimuli-responsive molecules displaying bistable molecular switches in solution can be classified in three main families: i) light-responsive molecules, ii) redox-responsive molecules, and iii) temperature-responsive molecules.

4.1.1. Light-Responsive Molecules

Light-responsive molecules have the ability to transform light energy into intelligent molecular functions encoded in the form of wavelengths, promoting significant macroscopic



Figure 11. Prominent examples of light-responsive molecules to be anchored on i2DMs with their corresponding photoisomers. A) Azobenzene, B) stilbene, C) spiropyran, and D) diarylethene derivatives.

effects.^[381] Light-driven bistable molecular switches—socalled photoswitches—are based on a phenomenon known as photochromism, which can be defined as a reversible structural transformation of the molecular skeleton induced by light irradiation that provides two different molecular forms (photoisomers).^[382] The resulting photoisomers exhibit not only different absorption spectra, but also physicochemical changes (e.g., geometry, rigidity, dielectric constant, etc.), which are, indeed, those physicochemical changes utilized to read out the system as two distinct states in a molecular binary logic element. In general, the main types of transitions of photoswitches rely on i) Z/E or *cis/trans* isomerization, ii) ring-opening/ring-closing, and iii) ring-flipping.

Amongst the wide variety of photoresponsive molecules presenting bistability in aqueous environments, derivatives of azobenzene,^[383,384] stilbene,^[385,386] diarylethene,^[387] and spiropyran^[388,389] are probably the most exploited ones. **Figure 11** illustrates the chemical formula and the photoinduced conformational changes of the selected photoisomers.

On the one hand, derivatives of azobenzenes (Figure 11A) and stilbenes (Figure 11B) undergo a change in their conformation from the most stable *E*-isomer form to the thermodynamically unstable *Z*-form under UV light irradiation, whose inversion equilibrium can be reversed upon visible light irradiation. On the other hand, diarylethenes (Figure 11C) and spiropyrans (Figure 11D) are another class of light-responsive molecules whose irradiation by modulating the light source induces a reversible ring opening and closing, promoting important physicochemical changes.

Alternatively, some nonplanar molecules like helix-shaped molecules (e.g., cethrene^[390] derivatives and sterically overcrowded alkenes^[346]) are capable of reversibly promoting a helical twist driven by a light source, which may result in a chiral inversion due to the disruption of symmetry (chiroptical switch). Finally, a recent work published by Gerwien et al. reported an eightstate molecular sequential switch through controlled rotations around three adjacent covalent bonds by alternating between photochemical Hula-Twist isomerizations and thermal singlebond rotations, demonstrating that one single molecule can promote eight different bistable forms.^[391]

4.1.2. Redox-Responsive Molecules

The main characteristic of molecular switches driven by an external electrical bias is that the molecular moiety must contain an electrically active group capable of undergoing conformational and/or chemical changes once the electrical input is received.^[392] For this type of molecular switches, two main groups of molecules can be considered: i) electrochemically redox active molecules and ii) electrochemically nonredox active molecules.

Regarding to redox active molecules, they have the particularity of possessing a redox active group capable of undergoing an electron transfer by adding or removing electrons, fact that can alter the electronic, optical, and magnetic properties not only of the molecules, but also their ensembles.^[393] Electron transfer, referred to as redox reaction, involves a process in which a species can either gain an electron leading to reduction (n-type or electron-acceptor species) or, conversely, release an electron to become oxidized (p-type or electrondonating species). Although redox-responsive molecules are typically driven by a physical stimulus (e.g., voltage), they might also be triggered by the action of a chemical agent (named as oxidants/reductants). Focused on physically stimuli-responsive electrochemically active molecules, the bistable molecular switch is obtained once the electrical bias enters the redox region, fact that usually alters the density charge of the molecular component, resulting in two or more distinguishable electrical states.^[54,394,395] Some eminent examples of electrochemically redox active molecules are derivatives of tetrathiafulvalene,^[396,397] ferrocene^[398,399] (and other metallocenes), anthraquinone,^[400,401] benzodifuran^[402] or viologen^[403,404] (Figure 12A), as well as more sophisticated molecules such as redox-active proteins,[405,406] transition metal complexes,^[407] macrocycles,^[408,409] and metalorganic frameworks.^[410,411] It is also worth to mention electrochromic molecules (or electrophores), a specific type of redox-responsive molecules that can reversibly generate optical variations (e.g., color, fluorescence, transparency) in response to an external bias potential, highlighting Prussian blue (hexacyanoferrate),^[412] diimides,^[413] and viologens,^[414] being the latest the only electrochromic organic molecule exploited in commercial applications so far.

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Figure 12. Representation of some stimuli-responsive molecules that could be grafted upon i2DMs to be triggered by an external electrical bias. Examples of A) redox active and B) nonredox active molecules.

Otherwise, some nonredox active molecules can also modify the electron transport when exposed to an electric field; nonetheless, that kind of switches are typically promoted in solid state, but not in solution. 4,4'-bipyridine and 1,4'-benzenedithiol,^[415] metaoriented diphenyl benzene^[416] and thiophene^[417] derivatives represent some examples of molecules exhibiting a particular phenomenon known as antiresonance features of destructive quantum interface, where changes in the molecular orbital energy levels relative to the electron Fermi level occurs after applying an external bias voltage, rather than carrier densities as in electrochemically redox active molecules.^[416] Another interesting type of electrochemically nonredox active molecule exhibiting bistability is the one reported by Liljeroth et al., who reported the tautomerization of two hydrogen atoms in the inner cavity of naphthalocyanine molecules.^[418] Tautomerization occurs when the two inner hydrogen atoms migrate in the framework of the cavity consisting of four nitrogen atoms (Figure 12B). This change is formally equivalent to the rotation of the molecule by 90°, promoting a substantial change in the tunneling current measured. Similar behavior was found for porphyrin molecules.^[419]

4.1.3. Thermal-Responsive Molecules

Thermal-stimuli systems have recently gained great interest in the development of biocarrier vehicles for controlled drug ADVANCED MATERIALS www.advmat.de

delivery.^[420] In general, molecular engineering has made it possible to devise thermally responsive materials (usually polymers) by selecting the molecular unit (e.g., monomers, reactive groups) that will mainly promote either a phase transition or a bond conversion into the system. There are several parameters that can be tuned to manipulate the temperature responsiveness, including molecular structure, functional groups, concentration, and/or hydrophilic–lipophilic balance.^[421] A large variety of synthetic (and also natural) molecular components have been utilized for temperature-responsive assemblies, which mainly include i) copolymers and ii) small organic molecules.

Several monomers display thermosensitivity once they polymerize, leading to a reversible structural phase transition driven by temperature change.^[422,423] In general, as temperature is increased, the degree of hydrogen bonding between the thermalstimuli moiety and water decreases, leading to a phase separation. Probably, the main term to take into in mind when selecting a thermoresponsive molecular moiety is its lower (or upper) critical solution temperatures, fact that can promote reversible desolvation (or solvation) upon working at temperatures below (or above) its critical transition temperature. These transitions may induce changes to their specific volume, mechanical properties and physical state, resulting in distinctive macroscopic states.^[424,425] Briefly, thermoresponsive polymers made of N-substituted acrylamide monomeres are one of the most studied polymers exhibiting lower critical transition temperaturesespecially poly(*N*-isopropylacrylamide) (PNIPAM), presenting a phase transition at 32 °C in aqueous solutions-,[426] while derivatives of sulfobetaine, such as polysulfopropylbetaine methacrylate and polysulfobutylbetaine methacrylate, present upper critical transition temperatures.[427]

Otherwise, it is known that some light-responsive molecular switches cannot be only erased (reversed) by light, but also with the help of an external thermal stimuli (heating), fact that usually leads to a thermal isomerization reaction. This is the case, for example, of azobenzene^[428] and spyropyran^[429] derivatives (see Figure 11) through a bond conversion, as well as overcrowded alkenes^[430] through a thermal helix inversion process.

4.1.4. Alternative Physical Stimuli-Responsive Molecules

Besides the aforementioned stimuli-responsive molecules, force and ultrasounds are another two types of physical inputs that can promote significant changes on molecules; however, they are rarely used for reading electronic outputs from molecular switches.

Force-responsive molecules are those that can exhibit a chemical (e.g., formation of a dipole moment or chemical bond activation/breakage) or physical shape change upon mechanical stress, such as compression, tension, pressure or shear. Prominent examples of mechanochemical molecules are spiropyrans activated into merocyanine by force—,^[431] dioxetanes,^[432] and diarylbibenzofuranones.^[433] Nonetheless, it is important to point out that breaking bonds usually lead to irreversible processes. From an electronic point of view, molecular assemblies formed by amino acid-based derivatives are of special interest in the field of piezoelectronics,^[434,435] since the induction of a dipole moment formation triggered by mechanical loads favors an electrically readable molecular switch.

Acoustic waves are a type of mechanical vibration that propagates through a medium by causing the compression and rarefaction of matter.^[436] Briefly, sonosensitizer is the term commonly utilized to describe ultrasound-responsive molecules/materials, which can produce reactive oxygen species when exposed to ultrasounds. Most of the molecular sonosensitizers are based on photosensitizers, including porphyrins, xanthenes, phenotiazines, and curcuminoids.^[437] Although attractive, ultrasoundresponsive molecules generally present poor water solubility and/or phototoxicity.

4.2. Molecular Switches Triggered by Chemical Inputs

Chemical inputs are associated to those molecules that can interact/respond to an external chemical or biochemical agent to promote a readable macroscopic change. In general, chemically stimuli-responsive molecules promoting bistable molecular switches can be summarized in two major families: i) molecules responding to chemical agents, including pHresponsive molecules and other ions beyond hydrogen ions (H⁺) and hydroxide ions (OH⁻), and ii) electrochemically active molecules suitable to be oxidized or reduced in the presence of an oxidant or reductant agent (viz., redox-responsive molecules, see Section 4.1.2). In addition, this section also includes another type of chemical stimuli, concretely supramolecular-responsive host-guest systems, where bistable molecular switches are promoted upon the cavity of a supramolecular recognition agent; nonetheless, it is important to point out that the resulting hostguest supramolecular complexes must be switched by the action of an additional external physical or chemical stimulus.

4.2.1. pH-Responsive Molecules

Molecular components containing acidic or basic groups are susceptible to interact with aqueous media depending on the pH of the solution, which in fact is related to their ability to react with hydroxide ions (OH⁻) or protons (H⁺), respectively. Thus, pH-responsive molecular switches are those that can promote a readable macroscopic change by alternately modulating the pH above or below the pK_a of the molecular unit. While the properties of optically active molecules can be tuned by varying the pH^[438-440] (typically yielding to an "on/off" pH sensor), other properties, such as hydrophilicity^[441] or conductivity,^[442] can be reverse by changing their charge state. In the latter, changes on the charges accumulated at the interface of electronic devices carrying pH-responsive molecules can be read out via double-layer capacitance by simply changing the pH of the electrolyte, fact that will promote the protonation or deprotonation of the sensitive molecular moiety.^[241,443] The most employed acidic molecules are those made of carboxylic acids, phosphoric acids, sulfonic acids, or boronic acids.^[444] Otherwise, main basic molecules are those containing in their skeleton Nrich groups with nonbonding electron pairs, such as amines,^[445] pyridines,^[446] imidazoles,^[447] piperazines,^[448] hydrazones,^[449] pyrrolidines,^[450] and morpholines.^[451] In addition, molecules

containing more than one pH-responsive group (e.g., amino acids like tryptophan, aniline, etc.) can be protonated and/or deprotonated by modulating the pH owing to the presence of both a carboxylic acid and amino group,^[452] making it possible to develop more complex systems.

Beyond protons and hydroxide ions, other molecular architectonics are susceptible to reversibly interact with other type of ions (e.g., alkali metals, alkaline earth metals, transition metals or halides).^[453] For example, calix[4]pyrroles represent an excellent model of anion receptor systems, in which their conformation can be switched from a more stable 1,3-alternate to a higher energy cone upon complexation with anions.^[454–457] In addition, as demonstrated in a photoresponsive TMH functionalized with a 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) molecular unit, this molecular component can interact with some hazardous metal ions (e.g., Cd²⁺), whose interaction can be reversed by the addition of a chelating agent as the EDTA.^[458]

4.2.2. Supramolecular-Responsive Host-Guest Systems

Host–guest motifs are likely the most recognizable manifestation of supramolecular chemistry. Supramolecular host–guest systems involve two molecular components (viz., host and guest molecules), which display a noncovalent interaction (e.g., H-bond, π -stacking or hydrophobic interactions) to form a supramolecular inclusion complex.^[459,460] Regarding to supramolecular-responsive host–guest systems, the main host molecules explored are those based on macrocyclic molecules containing inner cavities, which can act as container-shaped cavitands to entrap suitable active (guest) molecules according to the "lock and key" principle.^[461] Then, the supramolecular switch is driven by taking advantage of the responsiveness of the guest molecule to an external stimulus, leading to a molecular change (e.g., charge, conformation) that release the stimuli-responsive guest molecule from the supramolecular host–guest complex.

Amongst the different type of macrocycles (e.g., cyclodextrin (CD),^[462] curcubit[*n*]uril (C[*n*]B),^[463] calix[*n*]arenes,^[464] and pillar[*n*]arenes,^[465] see chemical structure in **Figure 13A**), CDs are the most utilized ones. Cyclodextrin is commonly composed of six, seven or eight glucopyranoside monomers (namely, α -CD, β -CD, and γ -CD, respectively) forming a truncated cone structure with an inner hydrophobic cavity and an outer hydrophilic surface.^[466] As illustrates in Figure 13B, five main types of guest molecules—1) ferrocene as redox-responsive,^[467] 2) imidazole as pH-responsive,^[468] 3) azobenzene as light-responsive,^[469] 4) bipyridine as ion-responsive.^[470] and 5) adamantane as thermalresponsive molecular units^[471]—are widely utilized to promote reversible supramolecular switches, since only one molecular state can fit the hydrophobic cavity of cyclodextrin.^[472]

Alternatively, C[n]B is another class of well-studied macrocycles that allows for hosting more than one guest molecule, making it possible to reach complex systems triggered by more than one external stimuli (known as orthogonal systems).^[367] For example, Tian et al. reported the suitability of C[8]B as a single supramolecular entity to simultaneously form host–guest heteroternary complexes with both redox-responsive (i.e., methylviologen) and light-responsive (i.e., azobenzene) molecules.^[473] ADVANCED SCIENCE NEWS ______ www.advancedsciencenews.com



Figure 13. A) Molecular structure of main cone-shaped macrocycles: cyclodextrins, curcubit[n]urils, calix[n]arenes, and pillar[n]arenes. B) Illustration of a reversible host–guest complex inclusion triggered by different external stimuli, highlighting the exemplification of ferrocene, imidazole, azobenzene, bipyridine and adamantane as redox-responsive, pH-responsive, light-responsive, ion-responsive, and thermal-responsive complexes, respectively.

4.3. Spin-Crossover Molecular Switches

The spin-crossover phenomenon describes the transition from a low to a high spin state by the help of an external stimulus, leading to the field of spintronics.[474,475] Spin-crossover molecules are those molecules presenting two bistable spin states-with different structural, magnetic, and/or electronic properties-which can be reversibly switched upon exposure to external stimuli, whether physical or chemical.^[476,477] In general, spin-crossover molecules are mainly composed of a central transition-metal ion, such as Fe(II),^[478] Fe(III),^[479] Co(II),^[480] Mn(III)^[481] or Ni(II),^[482] usually coordinated to N-donor ligands.^[483] While changes in pressure, light and temperature are the primary physical triggers that induce spin-crossover in organometallic molecules,^[484] chemical inputs encompasses both covalent and noncovalent interactions involving metal complexes with an analyte, complex dissociation, or ligand exchange in solution.[485,486]

5. Stimuli-Responsive i2DMs for Molecule-Programmable Nanoelectronics

The chemistry of molecular electronics for performing binary logic functions arose in the late 20th century with the pioneering work published by de Silva in 1993, who demonstrated the feasibility of analyzing a molecular optical switch in terms of the Boolean algebra for processing information, analogously to electronic systems.^[487] Since then, the readout of electrical signals between at least two well-defined molecular states (0, 1, also referred to ON/OFF or YES/NO) has been at the heart of the modern information.^[488,489] Due to the surface on any material can be directly interconnected with its surrounding medium, a simple change in the charge state or geometry of a molecule can have a significant impact on the performance of electronic devices. Further, molecular electronics are not only capable of changing properties upon demand (programming), but also sensing their environment (e.g., by employing host supramolecular components to tailor host-guest interactions with target molecules driven by

external inputs). Consequently, the use of molecular moieties as active electronic components offers great prospects not only for an eco-friendly miniaturization from a simple bottom-up chemical approach, but also for making them compatibles with biological systems. Particularly, the innovative combination of the outstanding properties of i2DMs—including atomic-level-thickness operation and reduced short-channel effect—^[490] with the inherent responsiveness of active molecules^[491] promises to overcome the barriers of electronics miniaturization and task-specific applications.^[15]

Although several pristine i2DMs have been applied to directly or indirectly perform some logical functions,[492-500] the implementation of stimuli-responsive i2DMs for electrically monitoring bistable molecular switches is still in a baby stage, which might provide new avenues toward the development of a new family of molecule-programmable nanoelectronics to advance in this conceptual crossover between materials chemistry and computation. What follows summarizes the recent advances of stimuli-responsive i2DMs to advance in the current post-Moore era, pointing out the monitoring of different molecular changes-triggered by an external stimulus of any nature-as an electrical output signal (e.g., electrochemical or electronic). It is worth to note that the integration of active molecules on electronic devices is not necessary realized to optimize charge transport, but rather to control it by implanting new properties to the material/device, enabling the performing of multifunctional tasks otherwise inaccessible for the pristine counterparts.^[501]

5.1. Electrically Monitoring Bistable Molecular Switches

In the last two decades, molecular switching has established itself as a pivotal approach for the development of a wide range of responsive materials and surfaces.^[502] Molecular switches can be described as single input–single output devices exhibiting reversible states triggered by an external stimulus (input), whose electrical dependence with regarding the molecular state can be utilized to electrically store information (output) in form of digital signals (i.e., zeros (0) and ones (1) in the binary code). Herein, the chemistry behind the following examples is based on reversible chemical reactions triggered by external stimuli (e.g., isomerization, protonation/deprotonation, cyclization, complex formation, redox reactions, or spin-crossover), where the different molecular states have a significant impact on the i2DMs electrical performance.

5.1.1. Stimuli-Responsive Xenes

Regarding to the use of stimuli-responsive Xenes for electrically reading molecular switches, Qiu et al. engineered a black phosphorous-based field-effect transistor (FET) functionalized with a diarylethene derivative to optically modulate the hole transport of FET devices.^[503] The different electrical states achieved derives from the different doping effect resulting from the ringopen/ring-closing of the bistable molecular photoisomers, fact that directly affects to the hole trapping process of the i2DM. Further, the photoresponsive black phosphorous-based FET system displayed excellent data-retention capacity at different current levels, opening new avenues toward its implementation as multilevel nonvolatile memory.

Su et al. evidenced an innovative mode of molecular switching, known as stereolectronic switching, which was displayed by employing oligosilanes^[504] and oligogermanes^[505]—considered here as analogous of silanane- and germanane-based Xanes, respectively—carrying methilthiomethyl linkers when probed by a scanning tunneling microscopy-based break-junction (STM-BJ) platform. In particular, both molecular systems exhibited two different conductance states (low *G* state and high *G* state), which were reversibly switched from a lower to higher conductance by elongating or compressing the molecular junction by few angstroms. This singular way of switching was ascribed to the strongly coupled Si–Si and Ge–Ge σ bonds that couple the stereolectronic features of the sulfurmethylene σ -bonds of the two terminal linker groups of the molecule.^[506]

5.1.2. Stimuli-Responsive TMCs

Several works reported by the research group of Samori have demonstrated the suitability of employing stimuli-responsive TMCs as active 2D channel materials for the fabrication of highperformance FETs, promoting a reversible optical control over the output current as a result of a molecular change.^[503,507-509] Briefly, in order to achieve efficient FET devices for performing binary logic operations, high charge-carrier mobilities, high onstate/off-state conductance ratios, high conductivity, and low offstate conductance are desirable.^[510] To reach some of these goals, different TMDs, including MoS₂ and WSe₂, have been considered for their functionalization with photoresponsive molecules, such as azobenzene,^[508] spiropyran,^[509] and diarylethene^[503,507] derivatives. In general, the resulting light-responsive TMD-based FETs provided two distinguishable photoswitchable charge trapping levels (electrons and/or holes) by alternating the light source with UV and visible light irradiation.

For example, the work carried out by Gobbi et al. revealed how the immobilization of spiropyran upon two different 2D materials (i.e., graphene, MoS₂) generate atomically precise superlattices, whose integration in FET devices provides a precise control over local charge carrier density derived from a lighttriggered structural reorganization (see Figure 14A).^[511] In addition, same author successfully interfaced different diarylethene derivatives on both WSe2- and black phosphorous-based FETs, demonstrating the unipolar modulation of either electron transport or hole transport, respectively.^[503] The photoinduced isomerization of diarylethene derivatives (open/closed forms) promoted different energy levels, resulting in a bistable molecular switch electrically monitored by means of charge transport. Alternatively, the suitability of fully exploiting ambipolar switching of charge transport in WSe₂ has been recently demonstrated via dual functionalization with two different photocromic molecules (n- and p-type diarylethene derivatives), each with specific energy levels engineered to selectively trap either electrons or holes from WSe₂.^[507] Interestingly, an optically switchable multilevel WSe₂based FET with ability to simultaneously modulate both electron and hole transport through remote light stimuli was achieved (Figure 14B).

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Figure 14. Electrically reading molecular photoswitches using stimuli-responsive i2DMs. A) Photoresponsive MoS₂-based FET device employing a spiropyran molecular derivative, showing how the light-driven isomerization favors a structural rearrangement. a1,a2) The scanning tunneling microscopic images of the molecular assemblies obtained before and after UV irradiation, respectively (note: images were obtained with alternative 2D materials like graphene). a₃) I_{DS}-V_{GS} performance of the photoresponsive MoS₂-based FET device after several cycles of UV-vis light irradiation, demonstrating the reversibility of the molecular switch. Adapted with permission.^[511] Copyright 2018, Nature. B) Energy level diagram of energy transport between WSe2 and the engineered photoresponsive diarylethene (DAE) derivatives, as both open (o) and closed (c) isomers. b1) Molecular and device structure of the i2DM-based FET. b₂) Electrical performance of WSe₂/DAE blend FET device showing the bistable molecular photoswitch by means of drain current (I_{de}) modulation over 10 illumination cycles with alternative UV (red shaded areas) and visible (blue shaded areas) light. Adapted with permission.^[507] Copyright 2018, Wiley.

Beyond photoresponsive molecules, alternative stimuliresponsive molecular components have also been explored to modulate the electronic properties of TMD-based devices. Zhao et al. functionalized MoS₂ with a redox-responsive molecule as ferrocene.^[512] After immobilizing the thiol-rich ferrocene on MoS₂ via vacancy engineering, the resulting stimuli-responsive was integrated in an FET to electrically read out a bistable molecular switch. Two distinct doping effects derived from its neutral or charged state were achieved, fact that efficiently tuned the electron density in MoS₂ (Figure 15A). Sideri et al. recently functionalized 1T-MoS₂ (the metallic phase counterpart this TMD) with a Hamilton-type host molecule (i.e., a barbiturate derivative) to explore supramolecular host-guest interactions with a redox-active ferrocene-barbiturate guest via H-bond www.advancedsciencenews.com

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Figure 15. Examples of redox- and thermal-responsive i2DMs exhibiting two electrical states. A) Schematic illustration of back-gate monolayer MoS_2 -based FET and its functionalization with a thiol-rich ferrocene to electrically read out a redox-triggered molecular switch. a_1) Back-gate transfer characteristics of the redox-responsive MoS_2 -based FET with regarding to the electrochemical state of ferrocene (oxidized/reduced) in the linear scale regime. Adapted with permission.^[512] Copyright 2020, Springer. B) Synthetic approach for the fabrication of stimuli-responsive MoS_2 with dual spin-crossover modulation (temperature and light). b_1) Electrical performance of the bistable molecular switch triggered by temperature. Inset: TEM image of the switchable molecular-based spin-crossover MoS_2 . Adapted with permission.^[514] Copyright 2021, Nature.

formation.^[513] The formation of the supramolecular complex leads to an electrochemical response derived from the presence of the redox-active guest molecule. Although this work does not directly present a molecular switch, the authors believe on the possibility of switching this material in the future by taking advantage of the temperature or solvent-dependent formation of that hydrogen bonds, which would make possible to achieve to distinguish electrochemical states. Torres-Canavillas et al. novelty engineered a switchable molecular-based spin-crossover MoS₂ material triggered by two different stimuli (light and temperature inputs), which serves to generate strain over the MoS₂ layer that promotes substantial and reversible changes in the electrical and optical properties of the i2DM.^[514] For this goal, MoS₂ was functionalized with 3-iodopropyl(trimethoxysilane) (IPTS, as molecular moiety) followed by $[Fe(Htrz)_2(trz)](BF_4)$ coordination polymer covered with a silica shell as spin-crossover unit, being Htrz: 1,2,4-triazole and trz: triazolate (Figure 15B). This work represents an excellent example of how a molecular moiety can serve to tune the strain applied on i2DMs and therefore, its electronic structure and electric conductivity.

5.1.3. Stimuli-Responsive MXenes

Moving to stimuli-responsive MXenes, Muñoz et al. reported the covalently anchoring of both a light-responsive molecule (i.e., azobenzene) and a pH-responsive molecule (i.e., tryptophan) upon $Ti_3C_2T_x$ –MXene through esterification chemistry for electrochemically monitoring bistable molecular switches on the top of a carbon-based electrode. On the one hand, the photo-driven inputs to isomerize the azobenzene molecule from the *E*-form to the *Z*-form resulted in two distinguished electrical states at the responsive i2DM/electrolyte interface that were successfully discerned via cyclic voltammetry.^[217] Remarkably, a dual modulation

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Figure 16. Reading molecular switches using responsive MXenes with electrochemical readout. A) Photoresponsive $Ti_3C_2T_x$ -based electrode employing an azobenzene molecular derivative. a_1) Cyclic voltammograms at the two different electrochemical states (before and after irradiation with UV light), with a_2) its corresponding molecular switchability after several cycles of UV/vis light irradiation. Adapted with permission.^[217] Copyright 2022, Royal Society of Chemistry. B) pH-responsive $Ti_3C_2T_x$ -based electrode employing tryptophan as active molecule, whose molecular switch resulted from the protonation/deprotonation of the amino group by modulating the pH of the electrolyte (before and after the pK_a). b_1) Real part contribution capacitance acquired at the two different pHs. Inset: control experiment using the pristine $Ti_3C_2T_x$ -MXene). b_1) Reversibility of the system by modulating the pH for several cycles. Adapted with permission.^[241] Copyright 2021, American Chemical Society.

of the electrochemical output signals was obtained by means of current intensity peak (I_p) and peak to peak separation (ΔE) by using a redox marker (i.e., $[Fe(CN)_6]^{3-/4-}$) as the electrolyte. Those electrochemical changes were ascribed to the molecular isomerization from the straight E-form of azobenzene to the Z-form counterpart after UV light irradiation, fact that hinders the accessibility of the redox marker to the electrode surface, and therefore lower $I_{\rm p}$ and higher ΔE values were yielded (Figure 16A). On the other hand, a multiresponsive Ti₃C₂T₂-MXene was synthesized by immobilizing an ammino acid as tryptophan, in which its pHresponsive properties were exploited to reach a bistable molecular switch once the Responsive MXene was immobilized on the electrode surface.^[241] In this case, the protonation/deprotonation of the amino group—induced by modulating the pH of the solution (lower and higher than the pK_2 of the NH₂/NH₃⁺ group) was monitored by means of real capacitance values (C_{re}) , since this parameter is directly related to the density of charges accumulated at the electrode/electrolyte interface (Figure 16B).

In addition, MXene-based i2DMs have also been interfaced directly or indirectly with stimuli-responsive polymeric moieties to electrically modulate electrical properties. On the one hand, Yu et al. prepared a MXene-based supercapacitor loaded with a thermal-responsive electrolyte (i.e., poly(*N*-isopropylacrylamide*co*-gly-cidylmethacrylate), PNGM) to meet the challenge of working at high temperatures.^[515] While at room temperature the ions of the electrolyte can migrate freely due to the hydrophilic nature of PNGM, at high temperatures the electrolyte forms a hydrophobic network that hinders ion migration. This heattriggered transition from hydrophilic to hydrophobic promotes significant changes on the electrochemical performance, yielding to 90% capacitance suppression when exposed to high temperatures. Sun et al. interfaced a stimuli-responsive polymeric moiety (PNIPAM) on MXene to prepare a hydrogel that response to two different inputs (i.e., light and force), resulting in two different outputs (i.e., thermal and electrical, respectively).^[516] Beyond the outstanding photothermal properties exhibited under NIR irradiation, the stimuli-responsive MXene-based hydrogel also presents significant changes on conductivity by means of resistance when exposed to diverse deformation inputs (e.g., bending, elongation, and compression), demonstrating excellent cycling stability and durability (**Figure 17**A).

5.1.4. Stimuli-Responsive TMOs/TMHs

Although the molecular functionalization of TMHs exhibiting switchability has been widely explored through the monitoring of optical outputs,^[517,518] the electrical readout of molecular switches is almost an unexplored field. To date, only a stimuliresponsive TMH based on a thermal input–electrochemical output system has been reported. Concretely, Dou et al. functionalized a CoAl-based layered double hydroxide material with a temperature-triggered polymer (i.e., PNIPAM) through a layerby-layer assembly technique upon the surface of an iron thin oxide electrode, and the reversibility of the thermal-stimuli system was electrochemically revealed using both cyclic voltammetry





Figure 17. Stimuli-responsive i2DMs carrying an active polymeric component (i.e., PNIPAM) exhibiting two different electronic states. A) Schematic illustration for the preparation of a force-responsive MXene-based hydrogel. Electrical performance of the stimuli-responsive MXene: a_1) real-time detection of human motions (finger bending and recovering) with a_2) its corresponding cyclability in 10 loading–unloading cycles. a_3) Relative resistance changes in response to compressive strain of 20%, 40%, and 60% with a_4) its corresponding cyclability in 10 compressing–recovering cycles. Adapted with permission.^[516] Copyright 2021, Wiley. B) Schematization of the synthetic approach carried out to realize an electronic device based on a thermal-responsive TMH for electrically monitoring a molecular switch. b_1) Intensity signals achieved at different temperatures. Inset: device switchability at two different temperatures (20 and 40 °C). Adapted with permission.^[519] Copyright 2012, American Chemical Society.

and electrochemical impedance spectroscopy tools.^[519] By modulating the temperature between 20 and 40 °C, two electronic states were observed by taking advantage of the contraction–expansion configuration of PNIPAM, resulting in low–high impedimetric values, respectively (Figure 17B). In addition, the sensibility of the electrochemical system toward the oxidation of glucose at the two different thermal states was also considered, demonstrating better results at 40 °C due to the better electrochemical behavior observed.

6. Conclusions and Outlook

The synthesis and exploration of alternative 2D materials (e.g., i2DMs), beyond graphene, has opened up new avenues toward the industrial implementation of unconventional 2D materialsbased nanoelectronics to be at the forefront of this emerging technological era known as post-Moore. 2D materials are named to address the current digital transition challenges of further miniaturization, resulting in more energy-efficient nanoelectronics displaying faster memory, computing, biosensing, and actuating capabilities. However, the large variety of 2D materials with their respective inherent characteristics and specific chemical reactivity clearly demand for general, robust, and straightforward functionalization strategies to make 2D materials functional for task-specific applications on-demand. Concretely, i2DMs, have been identified as promising candidates to lead this post-Moore era thanks to their outstanding and diverse physicochemical characteristics, as well as large surface-to-volume ratio that make them highly sensitive to changes in the surrounding environment. Although very promising from a scientific point of view, the reality is that the field of i2DMs is still in an early stage, and therefore further research must be focused on understanding the chemical reactivity of pristine i2DMs in order to introduce novel functionalities in a controllable manner by tailoring interactions between i2DMs and the moiety of interest.

In the last decade, molecular engineering has arisen as a powerful approach to fine-tune the physicochemical properties of 2D materials, making it possible to fulfill the central challenge of materials science by implanting a la cartè novel molecular features. Thus, molecular engineering has given light to integrate the functional programmability of molecular science into the next generation of nanoelectronics for digital processing and communication. In particular, by covalently anchoring active molecular components, novel and robust active/functional materials and devices (i.e., stimuli-responsive i2DMs) can be realized. Stimuli-responsive i2DMs can be seen as "intelligent" materials in which a controlled molecular transformation (e.g., conformation, charge state, etc.) triggered by an external input can be successfully transduced into electrical output signals, promoting the acquisition of programmable characteristics capable of performing binary logic operations at the molecular level. This performance is analogue to the one displayed by conventional Si-based semiconductor technology.

Herein, the molecular functionalization of pivotal i2DMs (e.g., Xenes, TMCs, MXenes, TMOs, and TMHs) has been indepth summarized, with main focus on covalently engineering stimuli-responsive i2DMs for the development of moleculeprogrammable nanoelectronics. Concretely, the assembly of active molecular moieties exhibiting bistable molecular switches at interfaces is particularly appealing, since the behavior of the resulting stimuli-responsive i2DMs can be simply manipulated by any type of external input (e.g., optical, electrical, pH, supramolecular, etc.) to address binary logic functions. In addition, from an operational point of view, electrical outputs constitute a convenient way to read out the state of the system. Consequently, research in combining i2DMs with molecular engineering will not only produce fundamental new knowledge, but also will play a key role in the development of the next generation of molecule-programmable nanoelectronics (e.g., memories, spintronics, logic gates, biosensors) for logical operation processing to be implemented in the near future. Interestingly, the implementation of stimuli-responsive i2DMs to read out electrical outputs has been highlighted with prominent examples of signal processing, demonstrating the suitability of transferring the characteristics of active molecules to i2DM-based nanoelectronics to speak the complex language of information technology. However, the practical integration and application of stimuliresponsive i2DMs as unconventional post-Moore technology for future nanoelectronics will depend on investing efforts on fundamental studies on various aspects of this research area, such as efficient molecular functionalization approaches to retain their signal transduction abilities.

Amongst the different families of i2DMs summarized in this Review, TMCs in general, and MoS₂ in particular, are by far the most explored ones for electrically reading molecular switches. This fact might be mainly ascribed to their commercial availability, low-cost production, inherent semiconductor nature, chemical stability, as well as versatility for covalently anchoring molecular components. Alternatively, black phosphorous has demonstrated to be the most explored member of Xenes' family thanks to its tunable bandgap and high carrier mobility. In this line, the promising achievements obtained by black phosphorous are promoting the active investigation of additional Xenes/Xanes, like gemanene/germanane and silicene/silicane. Although the family of MXenes is currently experiencing a boom in the field of electronics owing to their excellent electrical conductivity and suitability to be interfaced with molecular components, the tedious and often harmful synthetic methodologies commonly used for synthesizing MXens from MAX phases today constitute a fundamental obstacle that hinders the real implementation of MXenes. Regarding to TMOs and TMHs, their versatility and tunable properties, in combination with their range of electrical properties-from semiconductor to metal-make them attractive for a wide range of electronic applications; nonetheless, their molecular functionalization has been mainly used to explore optical approaches. Finally, the current molecular functionalization of i2DMs has been mainly restricted to photoresponsive molecules by taking advantage of their dopant effect and therefore, other on-demand capabilities must be explored via anchoring alternative stimuli-responsive molecular components. Indeed, the covalent molecular immobilization of ad hoc active components on i2DMs can provide a rational control over the nanoscale assembly of molecular switches, fact that can facilitate the better understanding of the mechanisms behind such macroscopic effects.

Overall, the covalent functionalization of i2DMs with molecular components displays promising application potential in several fields and provides a powerful platform for electrically monitoring bistable molecular switches. However, the implementation of stimuli-responsive i2DMs presents some challenges, including i) precise control over the external input, especially in real environments, ii) long-term stability (durability), iii) costly largescale production (scalability), and iv) versatility for different applications. To solve the aforementioned challenges, key solutions should be focused on i) developing at-point-of-use systems for real-time monitoring of molecular switches, ii) implementing covalent molecular functionalization methods to synthesize robust heterostructures in order to prevent leakage of molecular component, iii) improving manufacturing techniques like 3D printing by designing inks and filaments based on stimuli-responsive i2DMs, and iv) utilization of more than one molecular component to obtain multi-responsive i2DMs to enrich binary logic operations (e.g., orthogonal switches). Consequently, only the time will tell us whether these promising stimuli-responsive i2DMs will lead to the manufacturing of a new generation of digital devices for information processing.

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Conflict of Interest

The author declares no conflict of interest.

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