Strain Switching in van der Waals Heterostructures Triggered by a Spin-Crossover Metal–Organic Framework

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Van der Waals heterostructures (vdWHs) provide the possibility of engineering new materials with emergent functionalities that are not accessible in another way. These heterostructures are formed by assembling layers of different materials used as building blocks. Beyond inorganic 2D crystals, layered molecular materials remain still rather unexplored, with only few examples regarding their isolation as atomically thin layers. Here, the family of van der Waals heterostructures is enlarged by introducing a molecular building block able to produce strain: the so-called spin-crossover (SCO). In these metal–organic materials, a spin transition can be induced by applying external stimuli like light, temperature, pressure, or an electric field. In particular, smart vdWHs are prepared in which the electronic and optical properties of the 2D material (graphene and WSe$_2$) are clearly switched by the strain concomitant to the spin transition. These molecular/inorganic vdWHs represent the deterministic incorporation of bistable molecular layers with other 2D crystals of interest in the emergent fields of straintronics and band engineering in low-dimensional materials.

1. Introduction

The spin-crossover (SCO) transition represents one of the most spectacular examples of molecular bistability,[1] Fe(II) compounds formed by octahedral metal sites provide archetypical examples of this phenomenon. In these, a transition from a paramagnetic high-spin (HS) state with an open-shell configuration—($t_{2g}$)$_6$($e_g$)$_2$—to a diamagnetic low-spin (LS) one with a closed-shell configuration—($t_{2g}$)$_8$—(Figure 1a) may occur.[2] Since in the HS state the $e_g$ orbitals—which have an antibonding character—are occupied, the average metal–ligand bond length is higher for the HS if compared with the LS, thus leading to a compression/expansion of the metal site and, consequently, of the crystal lattice upon the spin transition.[3–5]

Although the SCO phenomenon has been widely explored at the nanoscale,[6] its deterministic combination with other 2D materials has not been studied yet. So far, just graphene grown by chemical vapor deposition or liquid exfoliated MoS$_2$ nanolayers have been combined with sublimated or drop-cast SCO nanomaterials.[7–10] While these previous approaches benefit of its easy fabrication process and scalability in terms of performing devices, they lack of the conceptual simplicity of a vdWH, being not possible to change at will the stacking sequence of the different layers involved.[11] In fact, the interplay between the SCO and 2D materials is currently under debate, being its origin attributed to different effects as chemo-electric gating,[7] modulation of the doping level,[8] spin-dependent polarizability,[9] or strain effects.[10]

As pointed above, the SCO phenomenon has been used to induce strain in 2D materials by linking in solution SCO nanoparticles on MoS$_2$ flakes.[10] Here, we introduce a novel technique for triggering strain on 2D materials by using thin SCO van der Waals layers. Current state-of-the-art regarding strain engineering on 2D materials includes the thermal variation or bending of the substrate where the 2D material is located,[12–15] inducing ripples and bubbles,[16,17] applying hydrostatic pressure,[18,19] or the use of piezoelectric and microheater actuators,[20–22] among others. Most of these approaches allow variation of the degree of strain, although they are technically complex and not easy to integrate, for example, with low-temperature measurements. Using thin SCO layers for introducing strain on 2D materials is as easy as fabricating a van der Waals heterostructure. Although the amount of strain in our approach is fixed and determined by the employed SCO system, the wide flexibility of coordination chemistry allows the degree of strain (volume change upon the spin transition) and transition temperatures to be tuned, offering a versatile toolbox of strain-inducing van der Waals materials.
Notice that so far 2D materials have been used as a tool for sensing the spin transition in these SCO compounds. In this work, we rather focus on the 2D crystal, studying the effect that this SCO compound has on its properties since, due to the insulating nature of the SCO, it is not expected that the 2D material modifies significantly the electronic properties of the molecular system. Nonetheless, we note that the fabrication of van der Waals heterostructures with graphene or other 2D materials can be employed for protecting these thin molecular layers upon, for example, laser irradiation. In particular, we explore how the electronic and optoelectronic properties of a 2D material are affected by the strain triggered by the spin transition. To reach this goal, we have prepared in a deterministic way vdWHs formed by SCO thin layers and inorganic 2D materials, such as semiconducting materials.
few-layers graphene (FLG), direct-bandgap semiconducting WSe$_2$ monolayer, metallic NbSe$_2$, and insulating hexagonal boron nitride (h-BN). As SCO system we have chosen the layered \{Fe-(3-Clpyridine)$_2$[Pt$^{II}$(CN)$_4$]\} metal–organic framework (Figure 1b), that presents a change in volume of ca. 8% upon the spin transition, with a thermal hysteresis centered at 150 K (see Section 6 in the Supporting Information).[23]

2. Results and Discussion

The SCO compound Fe-(3-Clpyridine)$_2$[Pt$^{II}$(CN)$_4$] can be mechanically cleaved to afford thin crystals, as performed with graphene or other 2D molecular materials.[24–26] The thermal bistability of this process can be tracked by optical contrast (Figure 1c) since the change in the lattice parameters concomitant to the spin transition results in a modification of both the thickness and the refractive index of the material.[23,27] Thus, a clear hysteresis loop can be observed (Figure 1c, central panel and in Movie S1, Supporting Information). Different SCO thin-layers are inspected (Section 3 in the Supporting Information), observing different spin-state propagation mechanisms. Typically, in the thickest SCO analyzed (≈1 μm), different domains are created, with even the appearance of cracks in the first thermal cycle, while in the thinner ones (ca. 300 nm) we observe a single domain wall propagation, being these layers

![Figure 2. Electrical characterization of an SCO/FLG vdWH (vdWH A.1 in the Supporting Information). a) Device with the transport configuration sketched showing the central SCO thin-layer and FLG across it. Scale bar: 5 μm. b) Artistic view of the vdWH. The SCO is represented in yellow, the FLG in purple and the contacts in gold. The use of a back gate voltage is sketched. c) Thermal dependence of the resistivity for the vdWH and the FLG. The transition temperatures for cooling (warming) are marked as blue (red) dashed lines. The blue (cooling) and red (warming) arrows indicate the hysteresis direction. d) Gate voltage dependence of the resistivity for various temperatures. e) Resistivity increment, Δρ(T,V$_g$), where Δρ(T,V$_g$) = ρ$_{warming}$(T,V$_g$) – ρ$_{cooling}$(T,V$_g$), as a function of the gate voltage and temperature.](image-url)
robust enough upon several thermal cycles. In addition, the spin transition can be also tracked by Raman spectroscopy, which shows an enhanced variation in the energy bands associated with the C–N and Fe–N vibrational stretching modes within the spin transition temperatures (see Section 2 in the Supporting Information).

Using these thin SCO crystals we have prepared SCO/FLG vdWHs, where the FLG is on top of the SCO, and investigated the electrical transport properties (Figures 2a,b). By performing 4-probe DC electronic transport measurements, we have characterized simultaneously the SCO/FLG vdWH and, as a reference, the isolated FLG (see Experimental Section). In Figure 2c we plot the thermal dependence of the resistivity, ρ. Considering the vdWH, a clear hysteresis loop is observed, where the transition temperatures (Tc) are highlighted with blue—cooling—and red—warming—dashed lines. Notably, this hysteresis only occurs for the vdWH whereas it is absent for the FLG case. The Tc values are in accordance with the reported temperatures for the bulk SCO compound, that are 141.4 K for cooling down and 164.5 K for warming up. The hysteresis loops are robust over several thermal cycles for the different prepared devices (see Section 4 in the Supporting Information). Moreover, we have investigated the influence of a gate voltage in the electrical response of the vdWH (Figure 2d). For addressing the influence of the SCO thin-layer, we compute the resistivity increment, Δρ(T,Vg), defined as Δρ(T,Vg) = ρwarming(T,Vg) − ρcooling(T,Vg). As shown in Figure 2e, the transition temperatures can be clearly observed for the vdWH, as a crossover between the blue region, where Δρ(T,Vg) = 0, and the red zone, where Δρ(T,Vg) ≠ 0. On the contrary, within the hysteresis loop, Δρ(T,Vg) exhibits a gate dependence with a minimum centered at around 20 V, coinciding with the charge neutrality point of the FLG. Regarding the FLG, no appreciable dependence is observed, being Δρ(T,Vg) zero, within the experimental error, for all the temperature and voltage range studied.

Thanks to the versatility offered by the vdWHs, different stacking configurations between the SCO and the 2D material are investigated. In particular, we consider the FLG placed above the SCO thin layer (in short SCO/FLG, vdWH type A) and the FLG placed below the SCO layer, in direct contact with the silicon substrate (FLG/SCO, vdWH type B). In addition, an intermediate h-BN layer is placed in between the FLG and the SCO layer (SCO/h-BN/FLG and FLG/h-BN/SCO for vdWH types C and D, respectively) to minimize proximity electronic effects present due to the contact between FLG and SCO. A hysteresis transition is clearly observed for all the vdWHs although the relative change in resistivity, Δρnorm, within the hysteresis depends on the stacking configuration. The highest Δρnorm values, up to 7%, are obtained for the SCO/FLG (Figure 3a), being reduced to a 2% in the reverse configuration, i.e., FLG/SCO (Figure 3b). The same trend is observed when an insulating h-BN layer is decoupling the FLG and the SCO, reducing Δρnorm from 1.5% in SCO/h-BN/FLG (Figure 3c) to 1.2% in FLG/h-BN/SCO (Figure 3d). In the same manner, we have placed a band metal, namely NbSe2. In the NbSe2-based vdWHs, the spin transition is not detected, regardless if the NbSe2 thin-layer is placed above (SCO/NbSe2, vdWH type E; Figure 3e) or below (NbSe2/SCO, vdWH type F; Figure 3f) the...
SCO thin-layer. The complete set of thermal cycles, different devices and geometrical factors can be consulted in Section 4 in the Supporting Information.

Overall, the SCO transition is clearly detected in a reproducible and robust way by transport measurements in the FLG-based vdWHs, yielding an enhancement (diminishing) of the resistivity while sweeping from HS (LS) to LS (HS). The magnetic transition increases the resistivity of FLG by about $\Delta \rho / \rho \approx 10\%$ (Figure 2). A plausible explanation of this effect is the presence of strains in the FLG due to the compression or expansion induced by the SCO, yielding to an estimated mean free path $\ell_r \approx 120$ nm, with a height modulation of $h_r \approx 1.8$ Å, and typical strains $\epsilon_r \approx \ell_r^2 / \ell^2 \leq 2\%$. We assume that the SCO induces or increases already existing ripples in the FLG, since many mechanisms that induce local compressions or dilatations lead to out-of-plane ripples. Although an electronic origin (produced by the change in the dielectric constant upon the spin transition, i.e., attributed to the different polarizabilities in the LS and HS caused by the structural variations concomitant to the spin transition) cannot be fully discarded, a strain effect is estimated to modify the conductivity stronger since strains couple to electrons by modifying the carbon-carbon distances which, in turn, change the hopping of electrons residing in $p_z$ orbitals in neighboring carbon atoms (see Section 4.5 in the Supporting Information for further details). In addition, note that the absolute values of the dielectric constant in SCO compounds are moderate, with a smaller change in those compounds undergoing the spin transition at lower temperatures. The resistivity change is larger when the FLG is on top of the SCO. This behavior is compatible with the effect of an in-plane and out-of-plane compression (expansion) while cooling (warming) when the SCO is underneath (SCO/FLG), but only an in-plane compression (expansion) when the SCO is on top (FLG/SCO). The same tendency is observed if an h-BN layer is placed between the SCO and the FLG but it is absent in the case of using the metal NbSe$_2$. This observation supports as well that electronic interactions or proximity effects do not seem to be the main origin of the interaction. More likely, we consider the volume change associated with the spin transition, which produces an effective strain in the 2D material that shifts the Fermi level. In accordance, no substantial variation in the conductivity is observed in a band metal such as NbSe$_2$ since the density of states does not vary drastically.

Interestingly, a measurable and hysteretic Hall resistance is observed when an SCO thin layer is placed above a FLG Hall bar (Figure 4a–c; see Experimental Section for fabrication...
details). This change upon the spin transition is also clearly appreciable when a gate voltage is applied (Figure 4d,e). In the FLG case, a residual, but non-hysteretic response is also found, suggesting the existence of a small residual magnetic field of a few Oe. The observed hysteretic effect in the vdWH can be understood in terms of strains associated to the magnetic transition of the SCO layer. These strains act like effective magnetic fields \[30\] on the electrons in the FLG. This additional field is to be added or subtracted to the residual magnetic field (depending on the valley in the FLG band structure), thus modifying the Hall response. The effect is small, but not negligible, and it changes slightly in different hysteretic cycles (see Section 4.3 in the Supporting Information). These results suggest that the strain induced magnetic field has a small value, as it reflects strain gradients which most likely average to zero, and that these strains change each time the sample is taken through the magnetic transition.

Photoluminescence (PL) is another physical property dramatically modified by strain.\[31\] In Figure 5a,b, a vdWH based on a WSe\(_2\) monolayer placed below an SCO thin-layer (WSe\(_2\)/SCO, vdWH type G) is shown. The PL thermal dependence for a reference WSe\(_2\) monolayer and the vdWH is presented in Figure 5c,d, respectively. At 200 K, the PL of the reference WSe\(_2\) monolayer and the vdWH are comparable, although the peak for the vdWH is slightly broader (see Section 5 in the Supporting Information). While cooling down, the PL peak narrows and shifts to higher energy values in the case of the WSe\(_2\) monolayer, as expected for a semiconductor. The same tendency is observed for the vdWH until the spin transition takes place and a considerable redshift and broadening of the peak occurs. The PL peaks can be fitted well by considering a Pearson IV distribution (see Experimental Section), as already reported for other transition metal dichalcogenide monolayers.\[32,33\] The obtained PL maximum and broadening, \(\Gamma\), are shown in Figure 5e and Figure 5f, respectively. For the reference WSe\(_2\) monolayer, the thermal dependence of the PL position and broadening is well described by the Varshni and Rudin–Reinecke–Segall laws\[34,35\] (see Experimental Section), respectively, in all the temperature range. For the vdWH case, the PL maximum position and peak broadening exhibit a clear hysteretic behavior when the

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**Figure 5.** Optical characterization of WSe\(_2\)/SCO vdWHs (third thermal cycle for the vdWH G.1 in the Supporting Information). a) vdWH formed by a WSe\(_2\) monolayer (purple dashed lines; thicker WSe\(_2\) is enclosed by blue dashed lines) below an SCO thin-layer (orange dash lines). Scale bar: 5 \(\mu\)m. b) Artistic view of the vdWH. Atoms are represented as black (carbon), green (chlorine), orange (iron), blue (nitrogen), gray (platinum), yellow (selenium) and dark gray (tungsten) balls. c,d) Normalized photoluminescence at different temperatures for a reference WSe\(_2\) monolayer (c) and the vdWH (d). For clarity, a vertical offset is added. The black dashed lines denote the maximum intensity position for the different spectra. e) Thermal dependence of the PL position for the vdWH and a reference WSe\(_2\) monolayer. Fits following the Varshni law are marked as dashed lines (for the vdWH, it is only considered the points at high spin). f) Thermal dependence of the line broadening for the vdWH and a WSe\(_2\) monolayer. Fits following the Rudin–Reinecke–Segall law are marked as dashed lines (for the vdWH, it is only considered the points at high spin). The cooling/warming direction is denoted with a blue/red arrow.
spin transition takes place. The broadening and shift of the PL peak are in agreement with the calculated evolution of the band structure for a WSe\textsubscript{2} monolayer under compressive strain, where there is a crossover of the minimum of the conductance band from $\Gamma$ to $\Lambda$.[38] In particular, from the PL measurements versus temperature (Figure 5), it is observed a bandgap diminishment of ca. 40 meV when comparing the reference WSe\textsubscript{2} with the vdWH. This value corresponds to a biaxial compressive strain of around 3%, as reported by Chang et al.[38] and matches the expected strain value from our SCO ($\Delta b/b = 4.4\%$ and $\Delta c/c = 2.5\%$, where $b$ and $c$ are the in-plane lattice parameters; see Figure 1b and Section 6 in the Supporting Information). Overall, similar trends are observed for various thermal cycles as well as in different vdWHs with the WSe\textsubscript{2} monolayer placed either above or below the SCO layer (see Section 5.3 in the Supporting Information). The broadening and shift of the PL peak is more significant when the WSe\textsubscript{2} monolayer is on top of the SCO thin-layer (SCO/WSe\textsubscript{2}, vdWH type I), probably due to the additional formation of out-of-plane ripples.[37] In addition, to disentangle the possible proximity and pressure effects, we place a thin h-BN layer between the WSe\textsubscript{2} monolayer and the SCO thin-layer, thus forming the sequences WSe\textsubscript{2}/h-BN/SCO (vdWH type J) and SCO/h-BN/WSe\textsubscript{2} (vdWH type H). In these cases, the analysis of the PL spectra is more complex since a significant inter-layer electron-phonon coupling occurs at WSe\textsubscript{2}/h-BN interfaces.[38] Nonetheless, the effects of the spin transition are noticeable although the overall effect is smaller than when no h-BN is placed (see Section 5.3 in the Supporting Information).

3. Conclusion

We have shown that the spin transition phenomenon occurring in molecular spin-crossover layers can switch the electrical and optical properties of 2D materials when assembled in van der Waals heterostructures. In particular, the electrical conductivity of FLG and the WSe\textsubscript{2} photoluminescence have been clearly modified by a thermal spin transition. This is attributed to the strain generated by the molecular layers due to the volume change concomitant with the spin transition. In the case of FLG this strain shifts the Fermi level, while in WSe\textsubscript{2} monolayers it changes the band structure. The present work incorporates spin-crossover layers as a novel building block able to induce strain in van der Waals heterostructures. Since the spin transition can be tuned by chemical design and triggered by a variety of physical stimuli, these molecular spin-crossover layers offer new routes for band engineering in 2D materials.

4. Experimental Section

Crystal Growth: [Fe(3-C\textsubscript{6}H\textsubscript{4}Py)]\textsubscript{2}[Pt(CN)\textsubscript{4}] was synthesized by adapting the procedure described by Martinez et al.[23] High-quality crystals of NbSe\textsubscript{2} were grown by chemical vapor transport (CVT) using iodine as a transport agent, as already reported by some of us.[39] Further characterization can be found in Section 1 of the Supporting Information.

vdWHs Fabrication: Bulk crystals of SCO, NbSe\textsubscript{2}, and natural graphite were exfoliated mechanically by the so-called “Scotch tape” method and placed on top of 285 nm SiO\textsubscript{2}/Si substrates using adhesive tape (80 µm-thick adhesive plastic film from Ultron Systems). As a prior identification, the obtained flakes were examined by optical microscopy (NIKON Eclipse LV-100 optical microscope under normal incidence). Atomic force microscopy images were taken with a Nano-Observer AFM from CSI Instruments. The vdWHs are placed on top of pre-lithographed electrodes (5 nm Ti/50 nm Au on 285 nm SiO\textsubscript{2}/Si from NOVA Electronic Materials, LCC) by the deterministic assembly of the flakes using polycarbonate, as reported by Wang et al.[40] using a micromanipulator. The whole process was performed under inert atmosphere conditions (argon glovebox). Regarding the Hall bar devices, mechanically exfoliated graphene flakes were deposited on SiO\textsubscript{2}/Si substrates and inspected in an optical microscope. The samples were then spin coated with poly(methylmethacrylate) (PMMA 495 kDa) and baked at 180 °C for 7 min. In order to shape the Hall bar configuration, the areas surrounding the Hall bar were exposed with conventional electron-beam lithography, and etched with O\textsubscript{2} plasma (exposed 20 s with a pressure of 0.05 mbar and a power of 25 W) in a plasma reactive-ion etching instrument (ICP Etch System S1500 from Sentsech). The remaining resist was removed with an acetone bath at room temperature for 3 min, rinsed with isopropanol alcohol, and dried with a nitrogen gun. For the electrical contacts of the Hall bar, the sample was spin coated on double-layer PMMA (495/950 kDa) and the metal contacts were fabricated by electron beam lithography techniques (5 nm Ti/50 nm Au). The lift-off was performed with acetone at room temperature.

Optical Contrast Measurements: Optical measurements were recorded with a camera (DCC1645C-HQ from Thorlabs) connected to an optical tube and a 20x objective. Temperature sweeps were performed with an open-flow nitrogen cryostat (manufactured by CryoVac), with top optical access (fused silica AR-coated window). The contrast was calculated as $C = (I_{SCO} - I_{substrate})/(I_{SCO} + I_{substrate})$, with $I_{SCO}$ being the intensity of the SCO and $I_{substrate}$ the intensity of the substrate.[39] Further details are given in the Section 3 in the Supporting Information.

Electrical Characterization: Electrical measurements were performed in a Quantum Design PPMS-9 cryostat with a 4-probe geometry, where the SCO and h-BN were sandwiched between two Au electrodes (5 nm Ti/50 nm Au on 285 nm SiO\textsubscript{2}/Si from NOVA Electronic Materials, LCC) and placed on top of pre-lithographed polycarbonate, as reported by Wang et al.,[40] using a micromanipulator. The measurement protocol was as follows: once the temperature stage. The measurement protocol was as follows: once the temperature
monolayers[32,33] (see Section 5 in the Supporting Information for further details). The thermal dependence of the PL maximum, \(E(T)\), was modelled by the Varshni law for a semiconductor[34] and the line broadening, \(\Gamma(T)\), to the Rudin–Reinecke–Segall law,[35] respectively. For the former,

\[
E(T) = E(0) - \frac{\alpha T^2}{T + \beta}
\]

while, for the latter,

\[
\Gamma(T) = \Gamma(0) + \sigma T + \Gamma' \frac{1}{e^{\frac{T}{\Delta T}} - 1}
\]

In the previous expressions, \(E(0)\) is the energy gap at 0 K; \(\sigma\) and \(\beta\) are fitting parameters related to the temperature-dependent dilatation of the lattice and the Debye temperature, respectively; \(\Gamma(0)\) is the broadening at 0 K; \(\sigma\) and \(\Gamma'\) reflect the interaction between excitons and acoustic and longitudinal optical phonons; \(\Delta T\) is the longitudinal optical phonon energy; and \(k\) is the Boltzmann constant.[32,33]

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

2D materials, molecular magnetism, spin-crossover molecules, van der Waals heterostructures

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