



Chemical Functionalization of 1H-MoS₂ for Programmed Modulation of Photoluminescence

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Semiconducting monolayer transition metal dichalcogenides (TMDs) such as MoS₂ possess exceptional properties that make them highly desirable in photonic and optoelectronic applications. The photoluminescence (PL) of MoS₂ is a valuable measure of its electronic and optical properties. Herein, chemical functionalization based on diazonium chemistry is used to modulate the PL of MoS₂ in a programmed fashion. Using PL mapping, it is demonstrated that binding of aryl units with electron-donating substituents leads to decreased PL, whereas electron-withdrawing substituents enhance PL compared to pristine MoS₂. This functionalization is utilized to selectively modulate radiative recombination in the basal plane and to demonstrate the

dependence of PL on the Fermi level. Raman spectroscopy corroborates the changes in the PL, and cryo-PL also confirms that the chemical functionalization proceeds without the creation of additional defects in the basal plane of MoS₂. The surface morphology of functionalized MoS₂ is characterized using scanning probe microscopy, which reveals the formation of well-defined one-nanometer-thick films. Electrical characterization of devices incorporating functionalized MoS₂ as the channel material reveals intriguing contrast to the PL trends, highlighting complex underlying mechanisms. Potential explanations for this divergence are explored, providing new insights into the electronic behavior of functionalized MoS₂.

1. Introduction

Layered materials, which exhibit highly anisotropic bonding, consist of ultrathin sheets made up of covalently bonded

atoms stacked together via weak intersheet interactions. Semiconducting layered materials, such as monolayers of transition-metal dichalcogenides (TMDs), hold promise in sustaining Moore's law by overcoming the scaling issues faced by silicon-based transistors. TMDs are semiconductors of the type MX₂, where each layer consists of a plane of transition metal atoms (Mo or W) sandwiched between two planes of chalcogen atoms (S, Se, or Te) in X-M-X form. The metal and chalcogen atoms are connected via strong covalent bonds, whereas the sheets themselves are held together through weak van der Waals (vdW) forces. Monolayers of TMDs exhibit a direct bandgap which is tunable from visible to near-infrared regions, a high yield of photoluminescence (PL), strong spin-orbit coupling, and high carrier mobilities, warranting applications in high-speed transistors, flexible electronics, optoelectronics, photonics, and spintronics.^[1]

Given its exceptional properties, stability, and abundance, MoS₂ remains the most intensively studied material among the TMDs. A monolayer of MoS₂, often termed 1H-MoS₂, has a direct bandgap of ≈ 1.9 eV and a red emission.^[2] Due to its semiconducting nature and high carrier mobility at room temperature, MoS₂ is being actively studied as a channel material in field-effect transistors (FETs). Highly efficient short-channel FETs with high on/off ratios have been demonstrated.^[3] Moreover, MoS₂ exhibits layer-dependent tunable bandgap and has strong interaction with light, which makes it a valuable material in photonics and optoelectronics research.^[4] The applicability of MoS₂ is further enhanced by its seamless integration into vdW heterostructures, where its properties can be combined with those of other 2D materials to realize applications in (opto) electronics^[5] and

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catalysis.^[6] Covalently linked heterostructures of graphene and MoS₂ have also been reported recently, further increasing the diversity of architectures and properties of MoS₂-based systems.^[7]

While the fundamental physics and the applications of MoS₂ and related 2D semiconductors are being intensively explored, there is also immense interest in tuning their properties to cater to the needs of different applications. The modulation of electrical properties is desirable for applications in (opto)electronics. Such modulation is often achieved *via* doping, which enables control over carrier density, conductivity, and contact resistance. Various doping strategies have been developed, including substitutional,^[8] electrostatic,^[9] and surface charge transfer^[10] doping. Among these, surface charge transfer doping (SCTD) using physisorbed molecular dopants is an attractive strategy. It provides a high degree of freedom due to the flexibility in dopant design *via* organic synthesis. Thus, the carrier type as well as the carrier concentration can be readily tuned *via* the choice of functional groups.^[11] Since physisorbed molecular dopants interact with the TMDs only through weak interactions, it is nondestructive and reversible compared to substitutional doping or doping *via* ion implantation, which may be accompanied by structural damage to the material. As a result, there has been a considerable surge of interest in molecular functionalization of TMDs and related 2D materials to modify and control their functional properties.^[12]

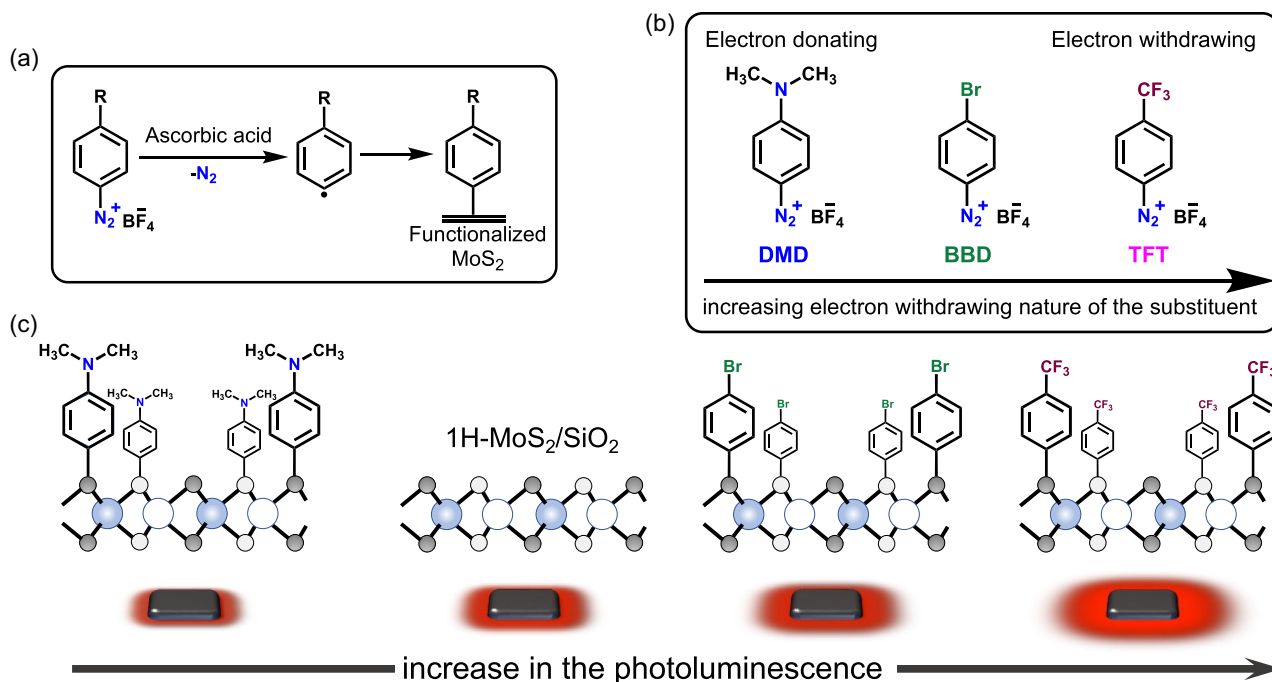
The covalent molecular functionalization of MoS₂ is more robust than that achieved *via* physisorption. However, TMDs are relatively inert. The chalcogen atoms that constitute the basal plane are saturated and hence are not highly reactive, whereas the metal atoms are buried underneath the chalcogen layer, making them inaccessible to chemical functionalization. Despite this,

various chemistries have been developed for attaching organic units to the basal plane of MoS₂.^[13]

Seminal efforts focused on covalent functionalization of both bulk polytypes of MoS₂, namely the metallic 1T^[14] phase and the semiconducting 2H phase.^[15] The strategies for functionalization of the 2H phase can be broadly classified into two categories. The first involves covalent bond formation targeted at defect sites such as edges and sulfur vacancies. It is achieved using thiols^[16] and dithiolenes.^[17] Since the intrinsic defect density for pristine MoS₂ is relatively low, these chemistries are often preceded by defect engineering,^[18] which makes the surface amenable to covalent functionalization. In the second category, the covalent bond is formed between the chalcogen atom and the organic moiety. The two most established chemistries are diazonium^[19] and maleimide chemistry.^[20] With these chemistries, organic units can be directly bonded to chalcogen atoms, thereby eliminating the need for defect engineering.

Despite the remarkable developments in molecular functionalization of TMDs in general, and MoS₂ in particular, there exist relatively few reports that demonstrate tunable doping. SCTD via physisorption of *n*- and *p*-type dopants has been employed for tuning the PL of MoS₂.^[11d] Thiol chemistry has been used for modulating the electrical performance of MoS₂ transistors via a choice of functional groups.^[21] A combination of diazonium chemistry and SCTD via physisorption has been used to demonstrate *p*- and *n*-type doping of WSe₂ FETs, followed by the realization of a *p*-*n* junction.^[22] Robust functionalization enabling control over carrier concentration and type is essential for (opto)electronic applications and insights into the molecule–material interface.

In this work, we use a self-limiting variant of diazonium chemistry^[23] (Scheme 1a) to demonstrate programmed modulation of



Scheme 1. a) A schematic showing the ascorbic acid-mediated covalent functionalization. b) Molecular structures of the diazonium salts used in this study. c) A schematic depicting the controlled modulation of the PL of 1H-MoS₂ using diazonium chemistry-based covalent functionalization.

the PL of 1H-MoS₂. Covalent functionalization of 1H-MoS₂ was carried out using three different diazonium salts (Scheme 1b) with varying degrees of (de)activating effect of the functional groups in the *para* position. We demonstrate that binding of aryl units with electron-donating substituents leads to decreased PL, whereas electron-withdrawing substituents enhance the PL in comparison to that of pristine MoS₂ (Scheme 1c). The modulation in PL is attributed to changes in radiative recombination processes within the basal plane due to Fermi level shifts from functionalization. The functionalized 1H-MoS₂ substrates were characterized via PL mapping. The density of binding and layer thickness were assessed using scanning tunneling-(STM) and atomic force microscopy (AFM), respectively. Raman mapping was used to substantiate the changes observed in PL upon binding of aryl units. X-ray photoelectron spectroscopy (XPS) and AFM-IR were employed for the chemical characterization of the functionalized layers. Electrical characterization of the functionalized MoS₂ layers was performed and compared with doping effects inferred from PL measurements.

2. Results and Discussion

Scheme 1 shows the overall strategy used for the controlled modulation of PL of 1H-MoS₂ via diazonium chemistry. The diazonium salts were chosen based on their different electron-donating and withdrawing ability (for synthesis and characterization details, see section S2 and S10 in the Supporting Information). **DMD** is

strongly electron-donating whereas **TFT** is strongly electron-withdrawing. **BBD**, in contrast, represents an intermediate case and is only weakly electron withdrawing. The functionalization experiments were carried out using 1H-MoS₂ transferred to SiO₂ substrates (see S1.2 in the Supporting Information). The binding of the aryl units to MoS₂ was achieved using a modified variant of diazonium chemistry which uses ascorbic acid as a reducing agent.^[23] Similar reductant-activated functionalization of the 1T'-MoS₂ has been reported in the recent past.^[14b]

Figure 1a shows the PL spectrum of pristine 1H-MoS₂ obtained using excitation by a 532 nm laser. The two main features of the PL spectrum are the so-called A (≈ 677 nm) and B (≈ 625 nm) peaks. These excitonic peaks are associated with the direct gap transition at the Brillouin zone K point and the energy difference corresponds to the valence-band splitting due to the strong spin-orbital interaction.^[2] The A peak exhibits higher intensity and comprises excitonic (I_x) and trionic (I_x^-) contributions, with only the latter showing dependence on the Fermi level. The changes in the PL were followed using a mapping approach where PL spectra were collected over an area of $20 \times 20 \mu\text{m}^2$ (289 point spectra) and plotted over an arbitrary X-Y scale. For each 1H-MoS₂ substrate, the PL mapping was carried out before and after functionalization.

Figure 1b shows the PL map of 1H-MoS₂ functionalized using **DMD** which carries the electron donating *N,N*-dimethylamino substituent. As evident from the map, the PL intensity decreases after functionalization with an electron-injecting moiety. The average peak excitonic PL intensity was found to decrease by

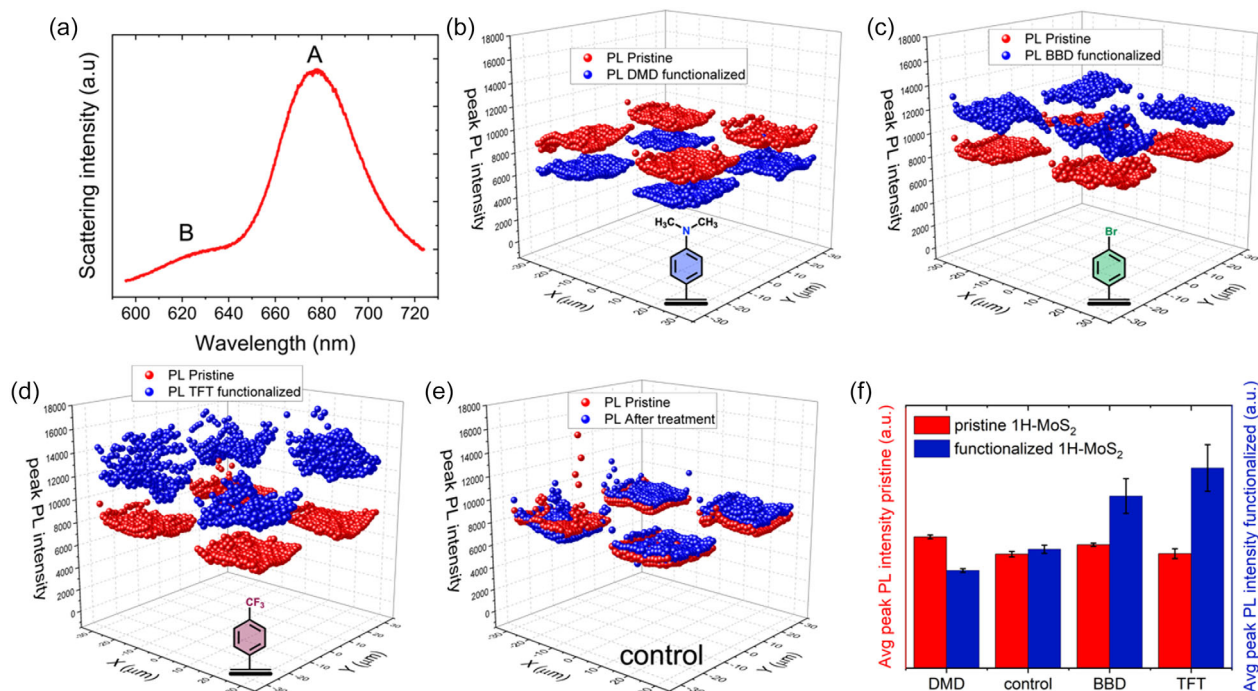


Figure 1. Controlled modulation of PL of 1H-MoS₂ via diazonium chemistry. a) PL spectrum of 1H-MoS₂ on SiO₂. b–d) Spatial maps of PL intensity before and after functionalization with b) **DMD**, c) **BBD**, and d) **TFT**. The spectra are collected over an area of $20 \times 20 \mu\text{m}^2$ (289 point spectra) and plotted over an arbitrary X-Y scale. Note that the PL intensity decreases after functionalization with **DMD** (b, factor change 0.7), whereas it increases to a different extent in the case of functionalization with **BBD** (c, factor change 1.4) and **TFT** (d, factor change 1.6). e) Spatial map of PL intensity before and after subjecting 1H-MoS₂ to the treatment with the reagents without the diazonium salt (control sample) showing no appreciable change in PL intensity. f) A plot showing the average change in the peak PL intensity upon functionalization with different diazonium salts with respect to the control sample.



a factor of 0.74 ± 0.02 after functionalization with **DMD**. On the contrary, the PL of 1H-MoS₂ functionalized with **TFT** (Figure 1d) was found to increase by a factor of 1.6 ± 0.1 . Finally, functionalization with **BBD** also led to an increase in the average PL by a factor of 1.4 ± 0.2 . The observed changes in PL following functionalization align with the electron-donating and electron-withdrawing nature of the aryl units bonded to the basal plane of MoS₂. Last but not least, when 1H-MoS₂ was subjected to the same chemical treatment without the diazonium salt, the change in the PL was found to be negligible (Figure 1e, a factor of 1.0 ± 0.1 change) before and after treatment indicating that the changes in the PL indeed reflect the functionalization by electronically dissimilar organic units. The average changes in the peak excitonic intensities for functionalized 1H-MoS₂ together with the control sample are presented in Figure 1f.

The experimentally observed changes in PL intensities can be understood by invoking fundamental principles of material PL. When a material is excited by light with a wavelength with energy higher than its bandgap, valence band electrons are excited to the conduction band, leaving an electron vacancy in the valence band. These transient charge-separated states of an electron in the higher energy band bound to its corresponding vacancy in the lower energy band are known as excitons. The recombination of these excitons may occur radiatively or nonradiatively. The radiative recombination of an exciton leading to the emission of a photon is the PL. Hence, the amount of excitons generated, and the efficiency of radiative recombination dictate the PL yield. 1H-MoS₂ is a direct bandgap semiconductor where the majority of carriers are electrons. Furthermore, it is also doped by the underlying SiO₂ substrate. These electrons can interact with excitons to form charged excitons or trions, which can in turn hinder radiative recombination.

We hypothesize that an electron-donating unit, such as **DMD** leads to the injection of electrons into the material, leading to a higher electron density in the basal plane. This in turn leads to an increased probability of trion formation and a concomitant decrease in the extent of radiative recombination, which is essentially reflected in the decreased PL intensity for 1H-MoS₂ substrates functionalized with **DMD** (Figure 1b). In contrast, functionalization with electron-withdrawing units such as **BBD** or **TFT** leads to a decrease in the number of excess carriers, thus lowering the probability of trion formation. This causes an increase in radiative recombination as reflected in the increased PL intensities (Figure 1c,d).

Further confirmation of the observed changes in PL intensities resulting from the binding of different functional groups was provided by Raman spectroscopy. The Raman spectrum of MoS₂ has two major features: the E_{2g} band and the A_{1g} band (Figure 2a). Of the two, the A_{1g} band is more sensitive to doping effects due to a stronger electron–phonon coupling in this Raman mode, whereas the E_{2g} band remains relatively unaffected. Injection of electrons into the basal plane (n-doping) is expected to manifest as an increase in linewidth of the A_{1g} peak, whereas removal of electrons (p-doping) leads to a decrease in linewidth.^[24] We account for these effects in our analysis by taking the ratio between the full width at half-maximum (FWHM) of the A_{1g} peak to that of the E_{2g} peak and by carrying out detailed

mapping of the surface. Panels 2b–2d in Figure 2 show the maps of the ratio of FWHM of the A_{1g} band to that of the E_{2g} for functionalized 1H-MoS₂. As evident from Figure 2b, for 1H-MoS₂ functionalized with **DMD**, the FWHM (A_{1g})/FWHM (E_{2g}) ratio was found to increase after functionalization relative to that for the pristine surface. We ascribe this increase to the broadening of the A_{1g} band due to the injection of electrons into the basal plane. In contrast, the ratio was found to decrease for **TFT** and **BBD**, which can be attributed to the sharpening of the A_{1g} band due to p-doping of the basal plane. The changes in the line widths for the control sample (Figure 2e) were negligible. Figure 2f presents the average change in the FWHM (A_{1g})/FWHM (E_{2g}) ratios which indicate that although the changes are small, they are in line with the anticipated effect of doping exerted by the chosen aryl units. For comparison of changes observed in the PL and Raman (FWHM) upon functionalization as a function of Hammett parameters, see Section S4, Figure S2 in the Supporting Information.

Having confirmed functionalization using spectroscopic methods, the morphology of the functionalized surfaces was characterized using scanning probe microscopy. To develop a molecular-level understanding of the grafting process, we first resorted to STM characterization. Given the challenges associated with STM imaging on single-layered 1H-MoS₂ samples (see the Experimental Section for details), functionalized synthetic MoS₂ crystals were used. Figure 3a–c shows STM images of synthetic (bulk) MoS₂ samples functionalized using **DMD** (Figure 3a), **BBD** (Figure 3b) and **TFT** (Figure 3c). For all diazonium salts, the STM data shows the presence of bright spherical features which we ascribe to covalently bound aryl units. Such features are hallmarks of covalently bound aryl units and have been observed previously in the case of covalently modified graphite^[23,25] as well as MoS₂.^[19d] The binding of the aryl units to the basal plane is random. We observed that continuous scanning of the functionalized surface resulted in the removal of the aryl units. Such scanning-induced de-grafting has been reported by us previously for covalently modified graphite^[25a] as well as MoS₂.^[19d] Thus, as argued previously in the case of covalently functionalized graphite,^[25b] we conclude that grafting densities observed using STM are underestimated. Nevertheless, based on the STM data, we conclude that grafting densities observed for **TFT**, **BBD**, and **DMD** are 3.5×10^{12} , 3.2×10^{12} , and 2.0×10^{12} units/cm², respectively.

The layer thickness of the films was obtained using AFM. Figure 3d–f shows AFM images with a granular morphology that is typical for covalently grafted films on MoS₂.^[19a,d] The thickness of the films was measured by removing a small part of the film using the AFM probe in contact mode and then measuring the difference in the height of the film against that of the MoS₂ surface. The film thicknesses obtained from such measurements were found to be ≈ 1 nm for **DMD** (Figure 3g), **BBD** (Figure 3h), and **TFT** (Figure 3i) indicating monolayer scale functionalization consistent with the self-limiting nature of the diazonium chemistry variant used here.^[23] Similar observations were made in the case of covalently modified 1H-MoS₂. AFM imaging of unmodified 1H-MoS₂ showed the presence of partial bilayer patches and treatment with diazonium salts led to a distinct change in

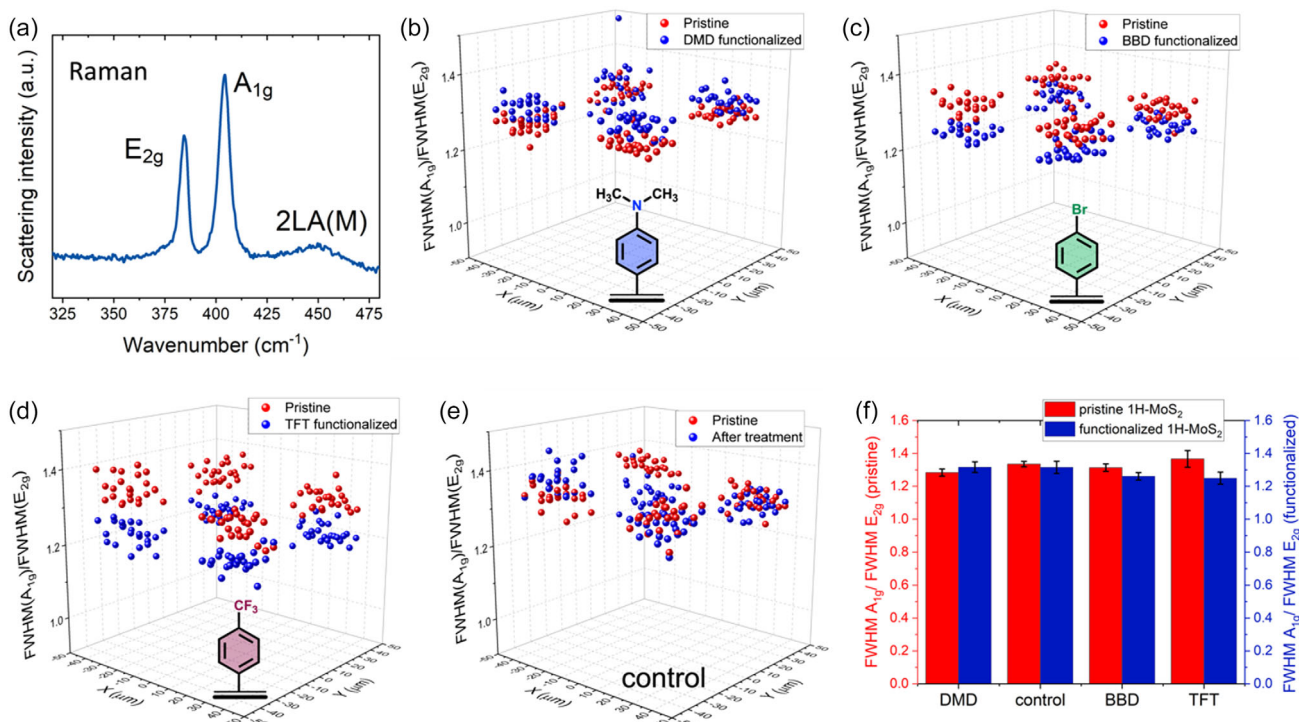


Figure 2. Raman spectroscopy characterization of functionalized 1H-MoS₂. a) Raman spectrum of 1H-MoS₂ showing the E_{2g}, A_{1g}, and 2LA (M) peaks. b–d) Spatial maps of the ratio of FWHM of A_{1g} peak to that of E_{2g} peak before and after functionalization with b) DMD, c) BBD, and d) TFT. The spectra are collected over an area of 20 × 20 μm² (25 point spectra) and plotted over an arbitrary X–Y scale. e) Spatial map of the ratio of FWHM of A_{1g} peak to that of E_{2g} peak before and after subjecting 1H-MoS₂ to the treatment with the reagents without the diazonium salt (control) showing no appreciable change. f) A plot showing the average change in the FWHM of the A_{1g} peak to that of the E_{2g} peak upon functionalization with different diazonium salts with respect to the control sample.

the roughness of the surface. In general, upon functionalization, the RMS roughness increased in comparison to that observed in the case of unmodified samples, and the surfaces showed similar granular morphology as observed in the case of functionalized bulk MoS₂ samples (see Figure S3 in the Supporting Information).

The functionalized 1H-MoS₂ on Si/SiO₂ samples were further characterized using XPS,^[26] which confirmed the presence of the respective elements in the reporter functional groups; fluorine in the sample functionalized with TFT, bromine in the sample functionalized with BBD, and nitrogen in the sample functionalized with DMD (see Figure 4a–c). Comparing the nitrogen and carbon regions (Figure 4c,d), there were significant background contributions from the unmodified substrate, leading to masking of relevant signals. By performing measurements at ten separate positions on the sample, however, it was clear that modification was present for all samples. The homogeneous equivalent composition showed fluorine to be 0.7 at% in MoS₂ functionalized with TFT while absent in other samples, bromine to be 0.7 at% in the sample functionalized with BBD while absent in other samples, and nitrogen to be present in the sample functionalized with DMD in a greater concentration than in the reference material (1.6 at% vs 0.4–0.9 at% in other samples). At the same time, the differences in Mo 3d and S 2p levels in all the samples remained negligible. A conclusive presence of C–S interaction could not be resolved due to a relatively high background C content (18–24 at% in all samples) (see Table S1 in the Supporting Information section S6). This carbon signal is unfortunately

unavoidable and may originate from the buried carbon in the Si/SiO₂ substrate or from polymer residues left by the thermal release (polymethyl methacrylate, PMMA) tape used to transfer 1H-MoS₂ from the sapphire substrate on which it is grown (see survey spectra presented in Figure S5 in the Supporting Information).

To avoid the presence of residual carbon content in the case of transferred MoS₂ samples, we also characterized functionalized bulk MoS₂ samples using XPS. The unfunctionalized bulk MoS₂ sample showed lower carbon content (see Supporting Information S6.3) than that observed in the case of the corresponding single-layer MoS₂ sample (Figure 4d). The XPS spectra of bulk MoS₂ functionalized with TFT and BBD revealed the carbon region of the functional layer as well. Various signals corresponding to the C1s environment could be identified in the XPS spectra presented in

Figure 4e,f. A C1s environment corresponding to the binding energy of >285 eV (deconvoluted spectra, green, Figure 4e,f) can be potentially ascribed to C–S interactions.^[19a] However, unlike previous reports,^[19a] the functionalization layer in this case contains carbon-halogen bonds, which also appear in the same region. As a result, the C1s environment corresponding to the binding energy of >285 eV could not be definitively attributed to C–S interactions.

The XPS data were further validated using nanoscale infrared characterization of functionalized MoS₂. Due to the extremely thin nature of the bound organic layers (~1 nm), conventional

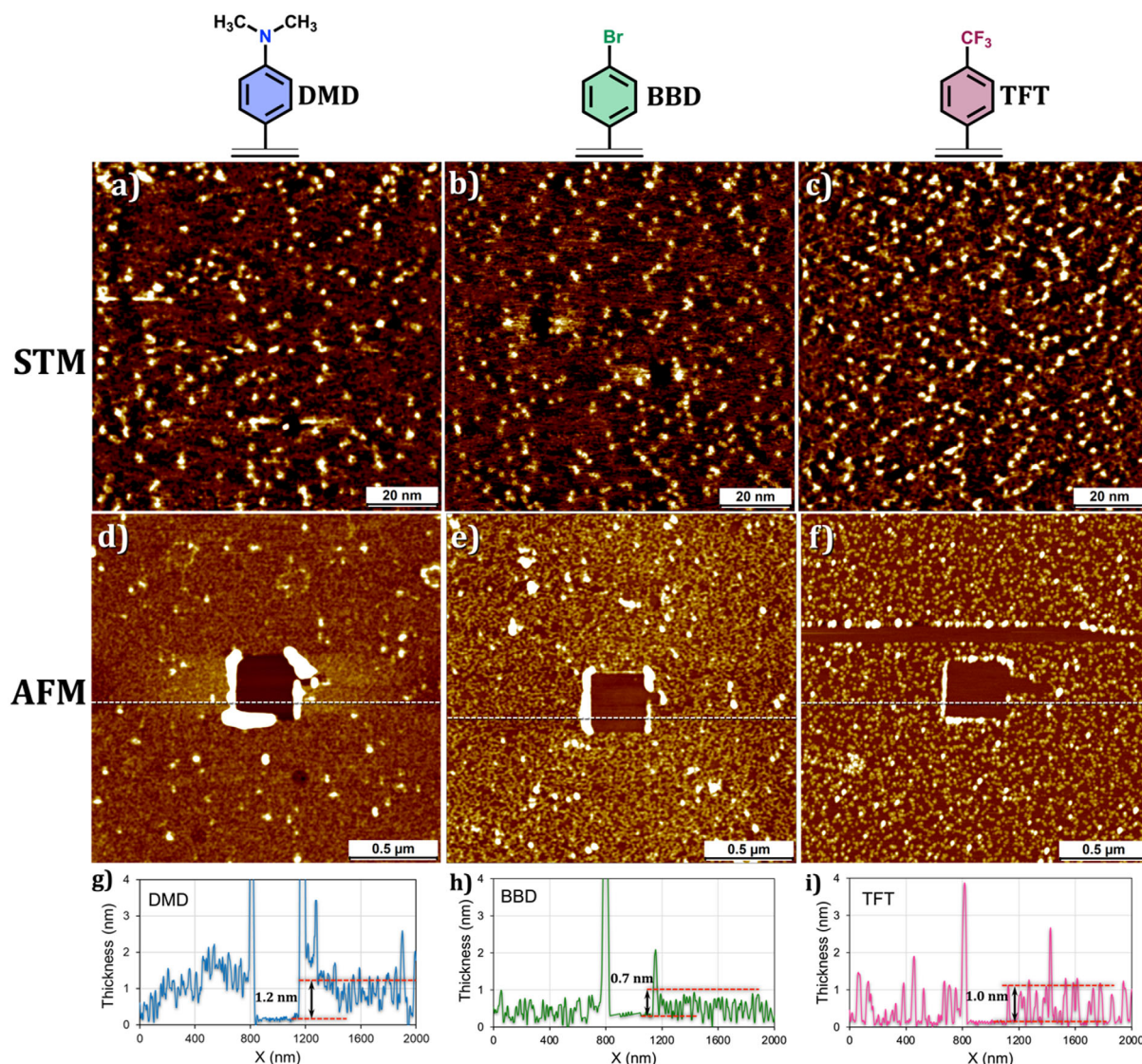


Figure 3. Scanning probe microscopy characterization of the covalently functionalized MoS₂ a–c) STM images of bulk MoS₂ functionalized using a) **DMD**, b) **BBD**, and c) **TFT**. Imaging parameters: a) $V_{\text{bias}} = -1.2$ V, $I_{\text{set}} = 0.03$ nA. b) $V_{\text{bias}} = -1.1$ V, $I_{\text{set}} = 0.04$ nA. c) $V_{\text{bias}} = -0.8$ V, $I_{\text{set}} = 0.06$ nA. d,e) AFM topography images of bulk MoS₂ functionalized using d) **DMD**, e) **BBD**, and f) **TFT**. The layer thickness was measured by removing a part of the organic film using the AFM tip in contact mode. The layer thickness was found to be around 1 nm in all cases as indicated in the corresponding line profiles g–i) measured across the scratched areas. See Supporting Information section S5, Figure S3 and S4 for the phase images corresponding to the AFM images and the scratch tests.

IR spectroscopy lacks the required sensitivity for functional group identification. Therefore, we employed AFM-IR, which combines the high spatial resolution and sensitivity of AFM with the chemical specificity of IR spectroscopy.^[27] Figure 4g–i presents the IR absorption spectra of the three functionalized surfaces, while the correlated topography and IR amplitude images can be found in the Supporting Information section S7, Figure S7. In general, the samples exhibit non-negligible absorption of IR radiation at wavenumbers corresponding to the reporter functional groups in the functionalized layer. Specifically, the **TFT**-functionalized sample shows absorption from the C–F stretch at 1350 cm^{−1} (8.6 ± 2.3 mV; see Supporting Information S7.1), while the **DMD**-functionalized sample exhibits absorption from the C–N stretch at 1180 cm^{−1} (6.3 ± 2.0 mV; see Supporting Information S7.1).

Due to limitations in the laser system of the AFM-IR tool, which only allows monitoring within the 930–1930 cm^{−1} region, we were unable to probe the C–Br stretching vibration, which appears at relatively low wavenumbers (≈ 650 – 550 cm^{−1}). All samples exhibited absorption at around 1100 cm^{−1}, which corresponds to aromatic C–H in-plane bending, although in the case of **TFT** functionalized sample, this absorption was relatively weaker and shifted. The absorption at this wavenumber follows the order of the surface density of diazonium islands (see Supporting Information S7.2). It is important to note that the relatively noisy spectra arise from the extremely thin functionalization layer (~ 1 nm), which inherently limits IR absorption.

The programmed modulation of PL in 1H-MoS₂ demonstrated above raises the question of whether the observed effect

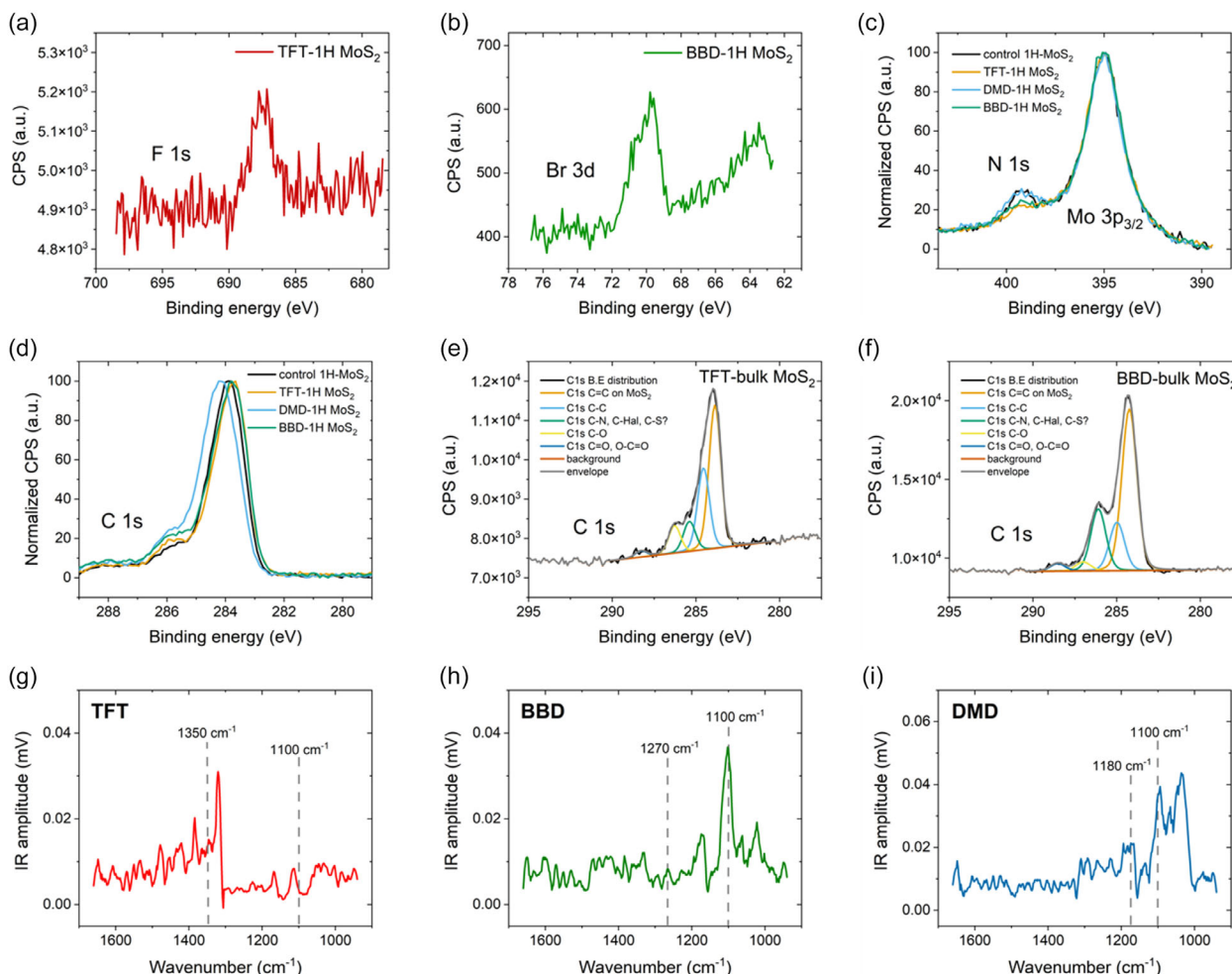


Figure 4. Chemical characterization of functionalized MoS₂. a–d) High-resolution XPS spectra of functionalized 1H-MoS₂ samples showing the a) F1s region for TFT functionalized, b) Br3d region for BBD functionalized 1H-MoS₂ samples. Panels c, d) show the N1s and C1s regions in the functionalized (TFT, BBD, DMD, and control) samples. These spectra contain background signals from C and N. Hence, a detailed elemental mapping was carried out (see Supporting Information section S6 for details). e, f) XPS spectra of bulk MoS₂ in the C1s region functionalized with e) TFT and f) BBD. g–i) AFM-IR spectra of g) TFT-, h) BBD-, and i) DMD-functionalized bulk MoS₂.

translates into doping of the basal plane of MoS₂. To investigate this aspect, we performed electrical characterization of functionalized 1H-MoS₂ integrated as the active element in two-point probe electrical devices (Figure 5a). To this end, an array of basic 2-probe Ni/Pd stack electrodes was contact printed over MoS₂ (Supporting Information section S1.3), followed by functionalization of MoS₂ using the electron-donating (DMD) and the electron-withdrawing (TFT) moieties. An additional device from the same production batch, which undergoes the same chemical treatment but without the diazonium salt, was used as a control for each functionalized sample. More than 200 devices with channel lengths ranging from 0.5 μm to 10 μm were studied on each sample.

Figure 5b demonstrates that devices functionalized with DMD do not exhibit any improvement in electrical properties. The threshold voltage (V_t), which is the potential at which a device turns on/off, is largely unaffected by functionalization. At the same time, the subthreshold swing (SS), which indicates the steepness of switching, and the on-current (I_{ON}) in these devices are found to deteriorate. In contrast, TFT functionalized devices

exhibited the expected doping effect, albeit with a decrease in I_{ON} (Figure 5c). The threshold voltage was found to shift by ≈ 10 V, which indicates *p*-type doping of MoS₂, which is in line with the electron-withdrawing nature of the functionalizing moiety. The SS of the device was found to be largely unaffected (see Section S8 in the Supporting Information).

To further understand the electrical characterization of functionalized devices and their potential dependence on the defects-to-exciton ratio, we resorted to low-temperature (cryogenic, cryo) PL measurements. Cryo-PL enables the study of low-binding energy processes, such as defect and shallow trap states, by minimizing thermal vibrations at cryogenic temperatures. This enhances sensitivity and reveals optical transitions that are often masked under ambient conditions. These passivating states can significantly suppress device performance. To this end, the cryo-PL spectra of samples functionalized with DMD and TFT, along with their respective controls, were measured under vacuum at temperatures ranging from 295 to 78 K.

For both the diazonium-functionalized and control samples, the PL intensity was found to increase with decrease in the

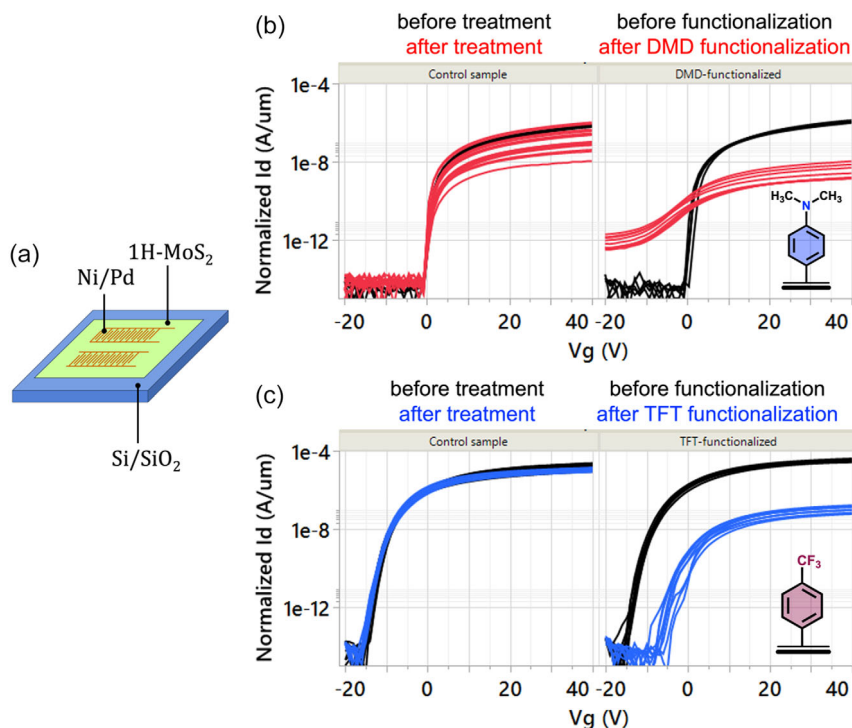


Figure 5. Two-probe electrical characterization of 1H-MoS₂ devices. a) A simplified scheme of the fabricated devices. b,c) Electrical (I–V) profiles of the devices before and after functionalization with DMD and TFT, respectively, along with their corresponding control sets. (after treatment = device went through the same chemical processing, but without the diazonium salt).

temperature, accompanied by a blue shift in the PL peak and a reduction in PL linewidth. These changes are consistent with the known temperature dependence of the PL of single-layer MoS₂.^[28] The increase in PL intensity is attributed to reduced thermal exciton quenching, which shortens radiative lifetimes and enhances radiative recombination. The blue shift in the PL peak is linked to changes in exciton binding energy and band structure, while the narrowing of the linewidth results from reduced thermal broadening and exciton–phonon interactions. Ambient temperature PL results align well with previous observations made for 1H-MoS₂ (Figure 1). The DMD-functionalized device exhibits a decrease in PL intensity (Figure 6a), whereas the TFT-functionalized sample shows no significant change in PL intensity (Figure 6b). These measurements are not quantitative due to uncertainty in the area masked by the contact-printed material. Nevertheless, the main objective of the experiment estimating the defect-to-exciton ratio yields similar results for both samples. At 78 K, the peak ratios of exciton (1.9 eV, ≈653 nm) and defect (1.7 eV, ≈730 nm) bands show no significant differences compared to the controls in either sample (Figure 6c,d; see deconvoluted spectra in Supporting Information Section S9). This confirms that the functionalization proceeds without significantly damaging the basal plane of MoS₂.

An overview of the electrical characterization (Figure 5) and cryo-PL measurements (Figure 6) shows that DMD-functionalized MoS₂, which exhibits significant PL modulation (Figure 6a,c) compared to the control, demonstrates poor electrical performance (Figure 5b). In contrast, TFT-functionalized MoS₂, which shows less pronounced PL modulation (Figure 6b,d), exhibits a threshold

change, suggesting no clear correlation between PL and electrical properties. At this juncture, it is worth mentioning a similar study carried out by Kim et al.^[21] where thiol-based functionalization was employed to modulate the electrical and optical properties of MoS₂. They observed a significant increase in current and carrier concentration with electron-donating thiol functionalization, while electron-withdrawing thiol functionalization resulted in decreased film conductance. This result was attributed to a shift in the Fermi level (E_x) caused by carrier injection. Although an opposite effect is observed in the present case (electron-withdrawing functionalization causing *p*-doping), a similar mechanism could be at play. Charge carrier injection after TFT functionalization can induce a shift in the Fermi level, which manifests as the threshold voltage (V_t) shift. However, semiconducting 2D materials like 1H-MoS₂ also contain mid-bandgap trap states.^[29] These trap states hinder the lowering of E_x upon functionalization with DMD, resulting in Fermi level pinning and counteracting the effects of electron donation. Other researchers have also identified these defect states as a major challenge in advancing 2D material electronics, with their elimination being crucial for improving device performance.^[30]

A possible explanation for the lack of correlation between PL and electrical measurements may lie in the fundamental differences between these probing techniques. Electrical measurements, which are performed under an applied bias (i.e., directional electric fields), probe ground-state charge transport properties such as carrier concentration and mobility. In contrast, PL studies probe the interaction between excited and ground states, typically under optical excitation.

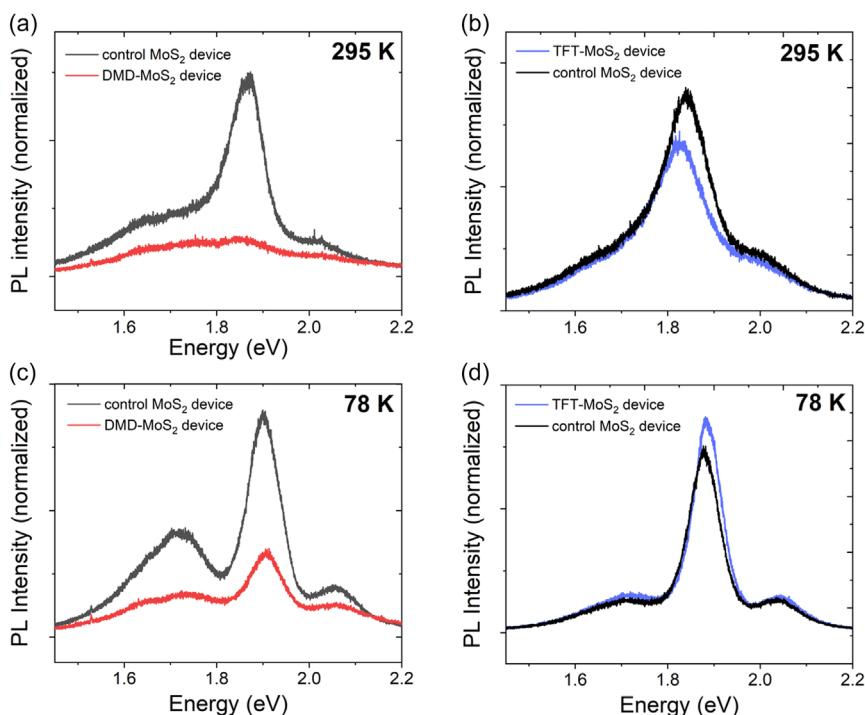


Figure 6. Cryo-PL characterization of functionalized devices. a,c) DMD-functionalized and control devices at room temperature and at 78 K, respectively. b,d) TFT-functionalized and control devices at room temperature and at 78 K, respectively.

The orthogonality of excited and ground-state wavefunctions ($\langle \Psi_1 | \Psi_0 \rangle = 0$) underscores their distinct nature, contributing to the divergence in observed outcomes. In essence, PL and electrical measurements offer complementary insights, each sensitive to different electronic processes in the material. Additionally, the nature of the charge carriers involved differs: PL involves excitons (bound electron-hole pairs), while electrical measurements involve free carriers influenced by external fields (e.g., gate or drain voltage). This distinction becomes particularly relevant in the case of covalently modified MoS₂, where surface states introduced by functional groups may selectively affect excitonic recombination without significantly altering bulk transport properties or *vice versa*.

3. Conclusion and Outlook

1H-MoS₂ is gaining interest as a potential replacement for Si in sub-5 nm transistors, driving efforts to modify and tune its properties. In the work presented above, we demonstrated controlled modulation of PL of 1H-MoS₂ by attaching *para*-substituted organic units to the basal plane of MoS₂. Our results clearly indicate that electron-donating substituents decrease PL intensity, and electron-withdrawing substituents increase it. Surface functionalization was confirmed using scanning probe techniques (STM, AFM) and further characterized by Raman, XPS, and AFM-IR measurements. Electrical characterization of functionalized MoS₂-containing devices revealed that electron-withdrawing functionalization induces *p*-doping, whereas electron-donating functionalization shows no significant effect, often attributed to Fermi level pinning. We also propose an alternative explanation:

electrical measurements probe the material in its ground state, while PL studies probe the excited state. The orthogonality of these states potentially results in noncorrelated observations.

Our work highlights the importance of recognizing the complementary nature of characterization techniques, which may yield correlated or anticorrelated results. Additionally, we confirm the electronic dependence of PL in 1H-MoS₂ and establish diazonium chemistry, facilitated by ascorbic acid reduction, as a reliable method for programmed modulation of PL in 1H-MoS₂. These findings are valuable for research into chemical modulation, sensing, and optical devices based on 2D materials.

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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: covalent functionalization · diazonium chemistry · MoS₂ · photoluminescence · transition metal dichalcogenides

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