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Controlled Covalent Functionalization of 2H-MoS₂ with Molecular or Polymeric Adlayers.

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Abstract: Most air-stable 2D materials are relatively inert, which makes their chemical modification difficult. In particular, in the case of MoS₂, the semiconducting 2H-MoS₂ is much less reactive than its metallic counterpart, 1T-MoS₂. As a consequence, there are hardly any reliable methods for the covalent modification of 2H-MoS₂. An ideal method for the chemical functionalization of such materials should be both mild, not requiring the introduction of a large number of defects, and versatile, allowing for the decoration with as many different functional groups as possible. Herein, a comprehensive study on the covalent functionalization of 2H-MoS₂ with maleimides is presented. The use of a base (Et₃N) leads to the *in situ* formation of a succinimide polymer layer, covalently connected to MoS₂. In contrast, in the absence of base, functionalization stops at the molecular level. Moreover, functionalization protocol is mild (occurs at room temperature), fast (nearly complete in 1h), and very flexible (11 different solvents and 10 different maleimides tested). In practical terms, the procedures described here allow for the chemist to manipulate 2H-MoS₂ in a very flexible way, decorating it with polymers or molecules, and with a wide range of functional groups for subsequent modification. Conceptually, the spurious formation of an organic polymer might be general to other methods of functionalization of 2D materials, where a large excess of molecular reagents is typically used.

Introduction

The ever-expanding toolbox of bidimensional materials and properties offers the promise of a technological revolution.^[1] Since the discovery of graphene,^[2] many other bidimensional materials have been isolated and characterized.^[3] Prominent examples now

span the whole range of band-gaps from hexagonal boron nitride (h-BN), an insulator (band-gap ca. 5-6 eV),^[4] transition metal dichalcogenides (TMDCs), which are semiconductors with band-gaps in the Vis-NIR region (1-2 eV),^[5] to black phosphorus (band-gap 0.3-2 eV).^[6, 7]

Within this toolbox of new materials, TMDCs show well defined bandgaps that make them particularly suitable for semiconductor technology.^[8-10] The development of reliable tools for the chemical modification of TMDCs is crucial to achieve their full technological potential.^[11-17] Decoration of TMDCs materials with molecular fragments via noncovalent approaches, mostly based on dispersion/solvophobic interactions, is relatively easy and has consequently led the way towards potential applications. For example, selective chemical sensors^[18, 19] and enhanced photodetectors^[20, 21] have already been described using this strategy. Methods for the covalent modification of TMDCs are much more scarce and nearly exclusively limited to the metallic 1T phase.^[22-26]

We have recently described a “click” chemistry protocol for the covalent modification of colloidal semiconducting 2H-MoS₂ and WS₂, obtained through liquid phase exfoliation (LPE) from the bulk.^[27-30] In our strategy, inspired by the many examples of thiolene chemistry in polymer chemistry and biochemistry,^[31-33] we exploited the soft nucleophilicity of sulfur to make it react with the prototypical soft electrophile, maleimides (**Figure 1**).^[34]

Here, we present a comprehensive study of the covalent functionalization of 2H-MoS₂ with maleimides. Via systematic changes to the different variables in the reaction conditions, we describe a reliable protocol for the molecular modification of MoS₂ with maleimides featuring a wide range of chemical functionalities. Our experiments reveal the formation of a covalently connected

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organic polymer adlayer when using increased amounts of molecular reagent in combination with a base.

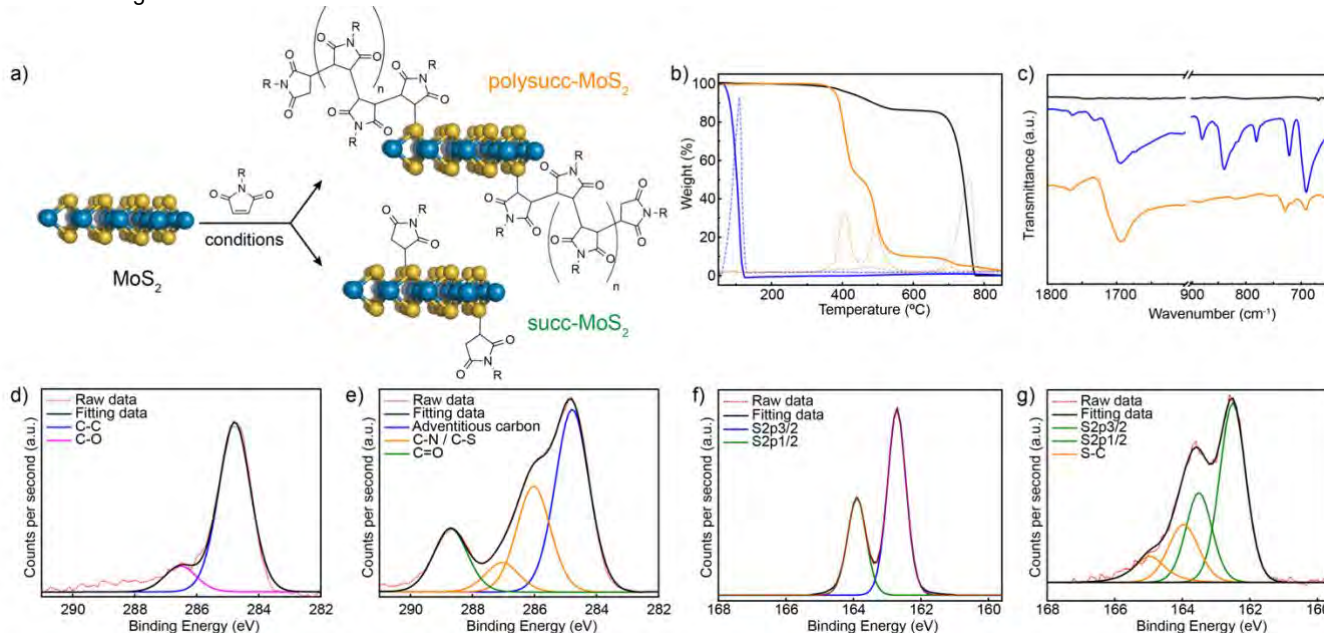


Figure 1. (a) General scheme of the two routes for the functionalization of MoS₂ with maleimides. b) TGA (Air, 10 °C min⁻¹) of exfoliated MoS₂ (black), Bn-polysucc-MoS₂ (orange) and Bn-mal (blue). c) ATR-FTIR of exfoliated MoS₂, Bn-polysucc-MoS₂ and Bn-mal (same colour code). d-e) XPS spectra of C core levels for exfoliated MoS₂ and Bn-polysucc-MoS₂. f-g) XPS spectra of S core levels for exfoliated MoS₂ and Bn-polysucc-MoS₂.

This unexpected formation of a polymer *in-situ* can be useful in certain circumstances and might be common to other functionalization protocols.^[35, 36] By removing the base from the reaction protocol, we obtain pure molecular functionalization.

Results and Discussion

Few-layers MoS₂ colloids were obtained through LPE in *N*-methyl-2-pyrrolidone, NMP, using an ultrasonic probe. In this case, we resorted to NMP instead of 2-propanol (*i*-PrOH)-water mixtures^[34] to increase the concentration of the colloids and facilitate characterization. Exfoliated MoS₂ was separated from non-exfoliated material using centrifugation. The formation of few-layer 2H-MoS₂ was proved, after redispersion in acetonitrile (ACN), by UV-Vis extinction, Raman spectroscopy, X-ray Powder Diffraction (XRD) and transmission electron microscopy (TEM, see Figures S1-4). The flakes showed layers with their larger dimension of 374±125 nm on average, as determined by TEM measurements.

The transfer to ACN of the exfoliated MoS₂ was done following a protocol described previously,^[37] then *N*-benzylmaleimide (Bn-mal) and triethylamine (Et₃N) were added and the mixture was stirred overnight (Figure 1). The mixture was washed with ACN and *i*-PrOH to remove all physisorbed Bn-mal, which was confirmed by UV-Vis of the residues (Figure S5). Moreover, the TGA profiles of the mixture without any washing could clearly differentiate physisorbed (weight loss at 170 °C) from covalently attached maleimide (weight loss at 390 °C, Figure S6). We first analysed the degree of functionalization varying degree of exfoliation, by fine-tuning the sonication conditions and centrifugation procedure, using TGA (Table S1). Unsurprisingly, we observed that, for materials with a higher degree of exfoliation (those obtained with longer sonication times and/or more intense

centrifugation conditions), a higher degree of functionalization was obtained. We also investigated the influence of reaction time, temperature, and the relative concentration of reagents on the degree of functionalization (Table S1). The main observations stemming from these studies can be summarized as follows: The reaction is fast, nearly complete after 1 h (52% functionalization by TGA, see Figure S7) and only increases to 66% after 16 h. Temperature studies were carried out from room temperature until reflux (Figure S8). However, the functionalization degree was reduced with increasing temperature, a result consistent with the stability of the dispersed MoS₂, which is less stable at higher temperatures. The use of different concentrations of MoS₂ had a significant effect on the surface functionalization, following the expected tendency, that is, the more the MoS₂ solution is diluted (i.e. the larger the excess of Bn-mal) the higher the degree of functionalization (Figure S9). Furthermore, similar variations were observed by reducing the concentration of Bn-mal (Figure S10). Decreasing the amount of Bn-mal results in a lower degree of functionalization. However, due to the small difference between 1 and 5 mmol of Bn-mal, we conclude that we are employing a large excess of Bn-mal. In fact, a quick calculation reveals that, even under the milder conditions used (entry 26, Table S1), we are using at the very least ca. 100 equivalents of Bn-mal with respect to S, assuming that all flakes are monolayer (our sample is mostly 5-10 layers) and that one out of six sulphur atoms can be reactive, to account for the steric hindrance of the organic addend. In agreement with this, we note that the degree of functionalization observed by TGA is too large to be compatible with the decoration of MoS₂ with molecular Bn-succ, which should be < 40% even assuming all flakes to be monolayer (see Table S2).

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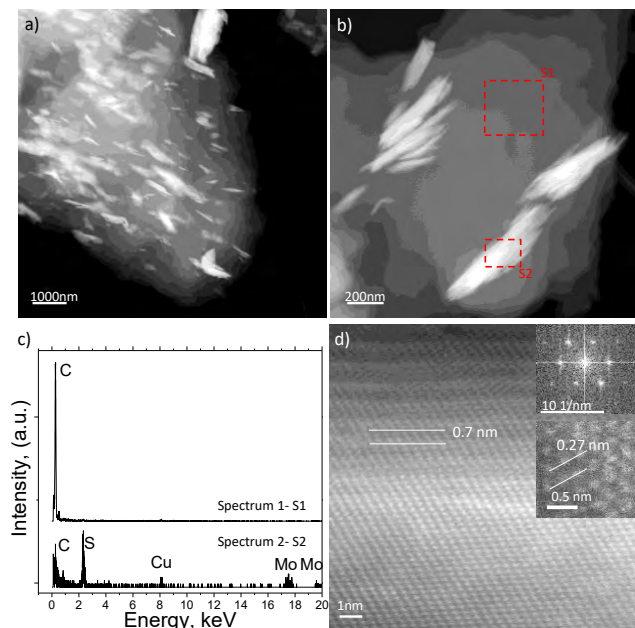


Figure 2. a-b) High-angle annular-dark-field scanning transmission electron microscopy (HAADF-STEM) images at different magnifications of polysucc-MoS₂ flakes. An organic layer with a less bright contrast than MoS₂ flakes was observed. c) Energy Dispersive X-Ray Spectroscopy analysis of dashed-red line areas in b). d) HR-HAADF-STEM image of polysucc-MoS₂ shows the interlayer arrangement. Insets, Fourier transform (FFT) pattern and atomic resolution image with interplanar spacing. Maleimide scope used for the covalent functionalization of MoS₂.

To gain further insight on the functionalization process we decided to fully characterize a sample which presented a 76% TGA weight loss (entry 27 in Table S1), comparing it with reference MoS₂, which was subjected to identical reaction and purification conditions in the absence of Bn-mal (Figure 1b). The slow decomposition of reference MoS₂ (black trace), observed between approximately 370 and 550 °C from the derivative, amounts to a total of 14% weight, and corresponds to the oxidation of MoS₂ due to the presence of air in the experiment;^[38] By comparing to the experiments in N₂ atmosphere (Figure S6), air, and the unfunctionalized reference, TGA suggests (Figure 1c), that the first weight loss of the functionalized sample (orange trace) at 390 °C can be attributed to defunctionalization of the attached molecule, the second at 450 °C to degradation of defective MoS₂ and the third one at 720 °C to degradation of all remaining MoS₂. The second weight loss is much more pronounced in the functionalized material compared to the pristine MoS₂. ATR-FTIR of the functionalized sample (Figure 1c) showed conclusive evidence of functionalization, like the presence of the main vibrational modes of Bn-mal like the carbonyl stretch (1714 cm⁻¹) and the disappearance of the alkene C-H bending mode (840 cm⁻¹ in Bn-mal), and the emergence of a S-C stretching mode (728 cm⁻¹) that confirms the covalent functionalization of the material through a new S-C covalent bond.^[34] X-ray photoemission spectroscopy (XPS) further confirmed the covalent attachment of the organic polymer (Figure 1d-g, Figure S11-12, Table S3). As a reference, the core level of C is centered at adventitious carbon (284.8 eV). We find clear differences with the control sample experiment (cs-MoS₂). The S 2p (162.7 eV) peak becomes broader, and a new component is required for spectrum fitting that corresponds well to the formation

of a S-C bond.^[39] The N 1s peak from the succinimide core, which is absent in the control MoS₂, is clearly visible at 400.7 eV upon functionalization (Figure S12). The presence of new bands in the carbon region is in good agreement with new components for C=O (288.7 eV) and C-S/C-N, (286.0-287.0 eV). XRD and Raman spectroscopy do not present a significant shift on the signals after functionalization (Figure S13-14). This is consistent with a picture in which only some of the surface S atoms are functionalized while the majority of the sample remains in the bulk (see Table S2), and where the functionalization does not significantly affect the electronic and structural properties of the MoS₂ lattice (i.e. no changes in crystalline polytype, significant doping, noticeable changes in the number of defects, etc.).^[34]

Some examples of high functionalization of MoS₂ are reported in the literature.^[26, 40, 41] In this work, the large degree of functionalization indicated by TGA experiments (up to 76%) differs markedly from that determined by XPS (12.8% of the S-C new component, that would correspond to a 23% weight loss in TGA, see Eq. S1, which is also in very good agreement with a very high yielding modification for 3-10 layers, see Table S2). Some studies pointed out the possibility of the homopolymerization and copolymerization of *N*-functionalized maleimides in the presence of bases.^[42-44] To investigate if the formation of polysuccinimides of this type was feasible under our reaction conditions, we prepared a mixture of Bn-mal (5 mmol) and Et₃N and stirred it overnight in ACN. After separation of unreacted Bn-mal, 1.5% of the initial weight was isolated as insoluble pink powder. MALDI-TOF analysis confirmed the formation of a polymer with a periodic repetition of 187 Da, which corresponds perfectly to the succinimide fragments of polysucc (Figure 1a). The formation of a Gaussian envelope from 2 to 10 kDa with a maximum peak at 4890 corresponds to 26 units of homopolymer (see Figure S15). Furthermore, ¹H NMR (400 MHz) experiments confirmed the disappearance of the alkene signals, and the appearance of signals at 4.61 and 4.40 ppm, that can be attributed to the new aliphatic protons. Moreover, all signals appear broadened, which is characteristic of the formation of high-molecular weight species (see Figure S16).^[45]

The strong evidence of formation of a S-C bond (ATR-FTIR and XPS) presented above indicates that MoS₂ is functionalized covalently with polysucc, rather than by physisorption of the polymer after formation in solution. A functionalization with polysucc would also be consistent with the large weight loss observed by TGA. AFM and STEM micrographs also support this hypothesis. In AFM we observe that the polysucc-MoS₂ flakes present roughness of a height of 15 nm, very similar to that of the pure polysucc (Figure S17). With the element-sensitive resolution of STEM, we confirm that we do not find self-standing polymer particles, but rather MoS₂ flakes surrounded by amorphous organic matter (Figure 2 a-b). EDS analysis also indicates that polysucc is grafted to MoS₂ flakes since the only presence of C was obtained at the less bright areas of the polysucc-MoS₂ HAADF-STEM image (Figure 2-c). Finally, the high resolution HAADF-STEM image of a representative MoS₂ flake reveals the periodic atomic arrangement of the MoS₂ layers, with an interlayer distance of 0.7±0.2 nm (Figure 2-d). On the other hand, the interplanar spacing was measured to be 0.27 nm according to the periodic pattern in the atomic resolution image, matching up with that of the (100) facet of MoS₂ (2.736 Å)^[46] and the fast Fourier transform (FFT) pattern (Figure 2d).

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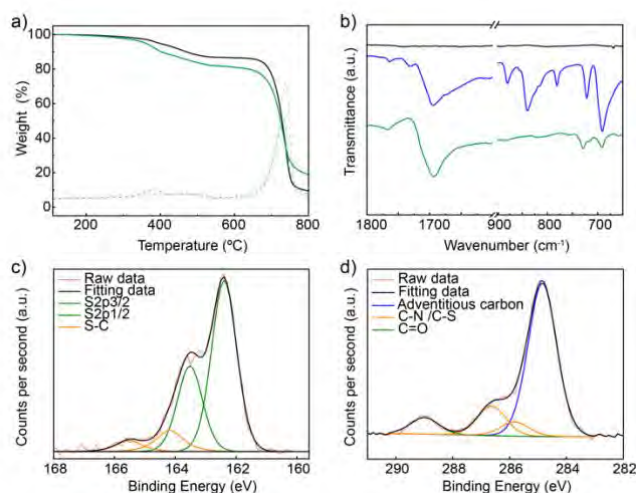


Figure 3. a) TGA (air, 10 °C.min⁻¹) of exfoliated MoS₂ (black) and Bn-succ-MoS₂ (green). b) ATR-FTIR of exfoliated MoS₂ (black), Bn-succ-MoS₂ (green) and Bn-mal (blue). c-d) XPS spectra of S and C core levels Bn-succ-MoS₂.

We note that grafting polymers onto the surface of 2D materials can be useful to decorate them with multiple functional groups, for instance to enhance binding to biomolecules for biosensing purposes,^[47-49] but is typically not the desired outcome when reacting molecules with nanomaterials.^[35] We therefore also studied how to control/prevent polymerization to obtain exclusively molecular functionalization. In this case, we tested experimentally that the polymerization of maleimide is not observable under our experimental conditions if a base is not present. **Figure 3** shows the characterization of Bn-succ-MoS₂. The weight loss of Bn-succ-MoS₂ observed by TGA dropped considerably, to 6% wt (Figure 3a). This is more in line with what can be expected for a rather effective surface reaction considering our degree of exfoliation (see Table S2). Again, we do not observe any weight loss before 300 °C meaning physisorbed Bn-mal was successfully removed during the washing step. In accordance with the lower amount of organic material, ATR-FTIR showed less intense signals of the material. However, the new C-S stretching mode (728 cm⁻¹) and carbonyl stretch (1714 cm⁻¹) are clearly observed (Figure 3b). XPS of Bn-succ-MoS₂ presents a broad band at the S 2p peak requiring a new component (6.8%) for the fitting that can correspond to S-C bond (orange, Figure 3c). Analysis of the C region is particularly informative: components for C=O (288.7 eV), C-S/C-N, (286.0-287.0 eV) are again needed for the correct fitting, but in this case, the relative intensity of the components are much smaller in accordance with molecular functionalization (Figure 3d). Finally, a N 1s peak that is not visible in the control sample is observed in the surface of the Bn-succ-MoS₂ material (Table S3). The TGA is identical for both control samples, with and without Et₃N, and the pristine material (see Figure S18). HR-HAADF-STEM images of pristine MoS₂, Bn-succ-MoS₂, showed how the crystallinity of the material was not modified with the functionalization (see Figure S19).

Lastly, we decided to test the scope and flexibility of these reaction conditions. First, we performed the reaction at different concentrations of Bn-mal (0.1 to 5 mmol). The functionalized MoS₂ showed a significant variation of the functionalization by TGA, from 2% to 6% (see Figure S20). This seems to be the upper limit for molecular functionalization. In fact, when the reaction was

left stirring for one month under otherwise identical conditions, we obtained a very similar degree of functionalization (6% wt comparing it with its pristine MoS₂, see Figure S21).

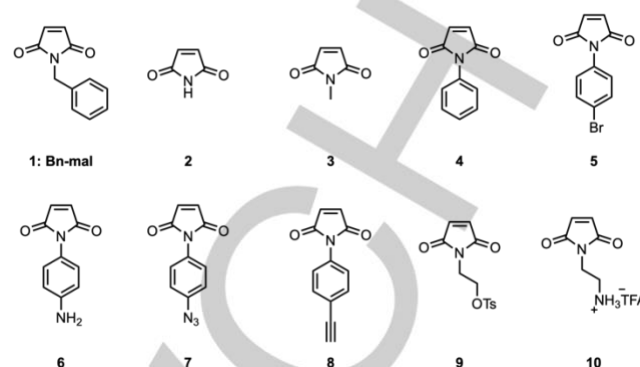


Figure 4. Maleimide scope used for the covalent functionalization of MoS₂.

The influence of different solvents was also investigated by performing the reaction in 10 more solvents, besides ACN, from the very polar methanol to the very unpolar hexane (see Table S4, Figure S22-23), including some that presented unstable dispersions (i.e. dioxane). A low degree of functionalization (< 2%) was found in polar protic solvents like methanol, ethanol or *i*-PrOH. This observation, together with the fact that the reaction works well in the absence of a base, points towards a radical mechanism for the 2H-MoS₂-maleimide reaction, instead of an anionic Michael-type addition.^[31, 32] Dichloromethane (8%) and chloroform (6%) both showed higher functionalization by TGA compared to ACN. However, the slope of the loss is not as well defined as in ACN (Figure S22), which might indicate that some physisorbed Bn-mal is still present, even after the washings. When the reaction was carried out in DMF we found 7% of organic material, comparable with ACN, but a more tedious cleaning of the material was required. Remarkably, ATR-FTIR confirmed the presence of the C-S stretching in all solvents, except dioxane (see Figure S23).

With the optimal reaction and purification conditions already determined, we tested the scope of the reaction using 10 different maleimides (**Figure 4**), some of which were intentionally selected to be used as chemical handles for further modification (5-10). Within experimental error, and considering the different molecular weights, we observe degrees of functionalization within the same order of magnitude (see **Table 1** and Figures S24-25) for all the maleimides, except **6**, which shows a much larger loading of organic material (16%). We explain this result noting that **6** features an aniline that probably acts as a base catalyst in the formation of a homopolymer, as shown above.

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Table 1. Summary of the characterization of the covalent functionalization of MoS₂ with different maleimides

n-MoS ₂	Weight loss [%]	ν C=O [cm ⁻¹]	ν C-S [cm ⁻¹]
Bn-succ-MoS ₂	6 ± 1	1714	728
2-MoS ₂	6 ± 2	1714	728
3-MoS ₂	1.0 ± 0.3	1702	728
4-MoS ₂	2 ± 1	1698	728
5-MoS ₂	8 ± 1	1704	731
6-MoS ₂	16 ± 1	1714	731
7-MoS ₂	2 ± 3	1714	-
8-MoS ₂	7 ± 3	1694	728
9-MoS ₂	13 ± 4	1714	731
10-MoS ₂	9 ± 3	1698	728

Conclusion

In summary, after disclosing that maleimides react with semiconducting MoS₂ and WS_{2,34} we now present a thorough study of the covalent functionalization of 2H-MoS₂ with maleimides. We report that the maleimide-MoS₂ click reaction is shown to be mild, fast, and extremely versatile. To achieve these conclusions, we explore changes in reagents, stoichiometries, concentrations, solvents, and temperature and expose that the use of a base (Et₃N) promotes formation of a polymeric maleimide adlayer, which is covalently attached to MoS₂. In the absence of a base, the functionalization stops at the molecular level. In both cases, the 2H polytype is preserved. Finally, we have investigated the scope of the reaction, showing a wide tolerance for different solvents and a broad range of functional groups. The fact that the reaction proceeds without a base, and particularly well in polar aprotic solvents, but is inhibited in protic solvents, suggests that it occurs through a radical mechanism.^[41]

Experimental Section

General procedure for Liquid-Phase Exfoliation (LPE) of MoS₂

1 mg/mL dispersion of MoS₂ in *N*-Methyl-2-pyrrolidone (NMP) was prepared in a 250 mL round-bottom flask by adding 200 mg of MoS₂ powder (<2 μm, 99 %) and 200 mL of NMP.

The mixture was sonicated in a Vibracell 75115 (VC 505 / VC 750)-Bioshock Scientific. The Ultrasonic Processor was used during for an hour, operating at the amplitude of 40 %, without pulse and using an ice bath to prevent the heating of the dispersion.

Afterwards, the black dispersion was divided into six falcon eppendorfs and centrifuged for 30 min at 2000 rpm (Allegra X-15R Beckman Coulter centrifuge, FX6100 rotor, 20 °C). Then, the supernatant (olive-color) was separated from the black sediment (non-exfoliated) by decanting and then it was filtered in a membrane filtration system (Omnipore 0.45 μm PTFE membrane filters, 45 mm in diameter). The membrane with the retained exfoliated MoS₂ was dispersed in acetonitrile and filtered again. This re-

dispersion process was repeated three times with 60 mL of acetonitrile (ACN) and three times with 60 mL of 2-propanol (*i*-PrOH).

General procedure for 2D-MoS₂ functionalization

The general procedure for the MoS₂ functionalization was performed by dispersing 6 mg of exfoliated MoS₂ in 10 mL of ACN with a brief sonication in a 20 mL vial. Then, the maleimide derivative was added and dissolved with vigorous stirring. The vial was closed with a lid and parafilm and allowed to react at room temperature for 16 h.

After that, the dispersion was filtered with Omnipore 0.45 μm PTFE membrane filters, 25 mm in diameter. In order to wash the sample, the filter with the material was redispersed in 20 mL of ACN, placed again in the filtration system and then the dispersion was filtered adding 40 mL more of the solvent. This process was repeated three times with ACN and three times with *i*-PrOH.

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Keywords: 2D materials • MoS₂ • covalent functionalization • maleimide • "click" chemistry.

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A comprehensive study of the reaction between 2H-MoS₂ and maleimides is presented. The use of a base leads to the formation of a succinimide polymer layer covalently connected to MoS₂. In the absence of base, functionalization stops at the molecular monolayer. The functionalization protocol is mild, fast, and very flexible.

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