HORIZON EUROPE PROGRAMME
HORIZON-CL4-2023-DIGITAL-EMERGING-01-33

GA No. 101135196

Developing New 2D Materials and Heterostructures for Printed Digital Devices

2D-PRINTABLE - Deliverable report

D2.4 – Second generation of discrete assemblies of 2DMs

Funded by
the European Union

Deliverable No.	D2.4	
Related WP	WP 2	
Deliverable Title	Second generation of discrete assemblies of 2DMs	
Deliverable Date	2026-08-31	
Deliverable Type	R	
Dissemination level	Public (PU)	
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Approved by	Jonathan Coleman (TCD) - Project Coordinator	2026-08-18
Status	Final	2026-08-18

Document History

Version	Date	Editing done by	Remarks
V1.0	2026-08-12	Antonio Gaetano Ricciardulli	draft
V1.1	2026-08-12	Paolo Samorì	
V1.2	2026-08-18	Antonio Gaetano Ricciardulli	final
FINAL			

Project Scientific Abstract

The 2D-PRINTABLE project aims to integrate sustainable large-scale liquid exfoliation techniques with theoretical modelling to efficiently produce a wide range of new 2D materials (2DMs), including conducting, semiconducting, and insulating nanosheets. The focus includes developing the printing and liquid phase deposition methods required to fabricate networks and multicomponent heterostructures, featuring layer-by-layer assembly of nanometer-thick 2DMs into ordered multilayers. The goal is to optimize these printed networks and heterostructures for digital systems, unlocking new properties and functionalities. The project also seeks to demonstrate various printed digital devices, including proof-of-principle, first-time demonstration of all-printed, all-nanosheet, heterostack light-emitting diodes (LEDs). In conclusion, 2D-PRINTABLE will prove 2D materials to be an indispensable material class in the field of printed electronics, capable of producing far-beyond-state-of-the-art devices that can act as a platform for the next generation of printed digital applications.

Public summary

Deliverable D2.4 addresses the molecular assembly of solution-processed two-dimensional materials at the nanosheet level. The central concept is to replace weak, uncontrolled contacts between neighbouring flakes with chemically defined junctions created by molecules carrying more than one anchoring group. The experimental work reported here validates this concept using benzene-1,4-dithiol (BDT) as a representative bidentate linker for transition metal dichalcogenide (TMD) nanosheets.

Liquid-processed MoS_2 and WSe_2 were used as model semiconductor building blocks. Molecular treatment was applied at chalcogen-deficient sites, allowing the same chemistry to contribute to vacancy healing and to the connection of adjacent flakes. Spectroscopic measurements on MoS_2 and WSe_2 confirm that the functionalization strategy can be transferred between chemically distinct TMDs. Repeating the local flake-linker-flake motif throughout a deposited film yields interconnected assemblies, as visualized by atomic force microscopy, while electrical measurements show that BDT treatment enhances charge transport through MoS_2 nanosheet networks. The molecularly assembled TMD platform was additionally combined with photoswitchable molecular functionality, producing wavelength-dependent electrical responses under UV and visible-light illumination.

The results establish a robust bidentate-linker strategy for second-generation 2DM assemblies and provide the chemical basis for extending this approach to heterostructures assembled from different nanosheet inks.

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Abbreviations & Definitions

Abbreviation	Explanation
2D	Two-dimensional
2DM	Two-dimensional material
TMD	Transition metal dichalcogenide
BDT	Benzene-1,4-dithiol
LPE	Liquid-phase exfoliation
AFM	Atomic force microscopy
PL	Photoluminescence
XPS	X-ray photoelectron spectroscopy
FET	Field-effect transistor

1 Introduction

Solution-processed 2D materials are attractive building blocks for printed electronics because nanosheets can be produced as dispersions and deposited by scalable liquid-phase methods. In contrast to continuous single crystals, however, a film assembled from individual nanosheets contains a large number of flake-flake interfaces. These interfaces can dominate charge transport, while defects exposed during exfoliation provide additional electronic scattering and trapping sites. Improving the performance of solution-processed 2DMs therefore requires control not only of the individual flakes but also of the junctions that connect them.

D2.4 targets a second generation of discrete 2DM assemblies in which molecular chemistry is used to define those junctions. Bi- or multidentate linkers are particularly relevant because a single molecule can carry two or more anchoring groups and can therefore connect more than one nanosheet. For TMDs, chalcogen vacancies provide chemically addressable sites for thiol-based functionalization. A dithiolated molecule can consequently serve a dual role: one thiol can react at a vacancy on one nanosheet while the second thiol remains available to connect to another nanosheet.

The experimental work presented here focuses on the use of BDT as a representative bidentate linker for MoS_2 and WSe_2 nanosheets. The chemistry is first assessed at the level of molecular functionalization and then at the level of the assembled film, where repeated flake-linker-flake junctions generate interconnected TMD networks. Beyond improving nanosheet connectivity, the molecularly engineered assemblies were further post-functionalized with photoswitchable molecules, introducing an additional optically addressable functionality and enabling wavelength-dependent modulation of the electrical response under UV and visible-light illumination. In this way, the work progresses from chemically defined nanosheet junctions to multifunctional 2DM assemblies in which interflake coupling and external-stimulus response can be introduced through distinct molecular components.

2 Methods and core part of the report

2.1 Preparation of the 2DM building blocks

MoS_2 and WSe_2 nanosheets were prepared by liquid-phase processing followed by controlled centrifugation and redispersion. Processing conditions were adjusted to obtain stable dispersions while controlling flake dimensions and preserving the semiconductor phase. The representative MoS_2 population had a typical lateral size of about 2 µm and an average thickness of approximately 5 nm. For WSe_2, typical lateral sizes were about 200 nm, with thicknesses in the 5–20 nm range.

2.2 Molecular-linker strategy

Thiolated aromatic molecules were investigated as molecular modifiers of the exfoliated TMDs. BDT was selected as the representative bidentate linker because it contains two terminal thiol groups. The functionalization scheme is shown in Figure 1a. The strategy exploits chalcogen-deficient sites on the TMD flakes: molecular attachment at these sites provides a route to defect passivation, while the second thiol functionality enables coupling to an adjacent nanosheet.

2.3 Assembly procedure

TMD inks were deposited using solution-based coating approaches. Interconnected assemblies were then constructed through alternating nanosheet deposition and molecular-functionalization steps. This procedure allows the local molecular junction to be repeated throughout the film. Different TMD inks can be selected or combined during deposition, making the chemistry compatible with compositionally varied 2DM assemblies.

2.4 Data analysis

OriginLab software was used to carry out data analysis. NanoScope software from Bruker was used to preform AFM data treatment.

3 Results & Discussion

3.1 Results

3.1.1 Molecular functionalization across different TMDs

The molecular functionalization strategy was examined on both MoS_2 and WSe_2. Figure 1a summarizes the functionalization concept. For MoS_2, the comparison before and after BDT treatment is shown by Raman spectroscopy (Figure 1b), photoluminescence spectroscopy (Figure 1c) and Mo 3d XPS (Figure 1d). The same approach was then applied to WSe_2: Figure 1e shows the Raman comparison, while Figures 1f–h show the corresponding W- and Se-related XPS regions. These measurements support successful molecular functionalization and are consistent with the defect-healing and electronic-property modulation observed after thiol treatment.

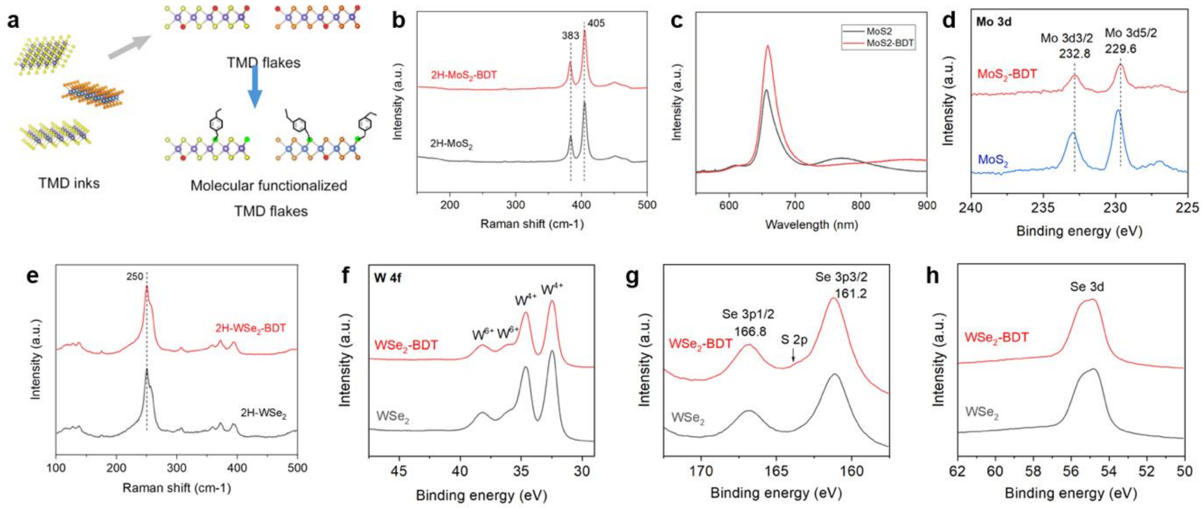

Figure 1. Molecular functionalization of solution-processed TMD flakes. (a) Schematic of the functionalization strategy using thiol-containing molecules. (b–d) Raman, photoluminescence and Mo 3d XPS comparisons of liquid-processed 2H-MoS_2 before and after BDT treatment. (e) Raman spectra of 2H-WSe_2 before and after BDT treatment. (f–h) XPS regions of BDT-treated and untreated 2H-WSe_2, including W 4f and Se-related core levels.

3.1.2 From discrete flake junctions to interconnected assemblies

The key step in D2.4 is the creation of molecularly defined connections between individual nanosheets. Repetition of this flake-level linking motif during deposition progressively builds up extended, interconnected networks. Figure 2 follows this process across successive deposition/functionalization stages. Figure 2a shows the initial TMD-flake state. After introduction of the molecular linker, the schematic and AFM image in Figure 2b show the formation of a more interconnected assembly. Repetition of the deposition and functionalization sequence further increases the density of linked nanosheets, as shown in Figure 2c. The resulting film is therefore built from repeated local flake-molecule-flake junctions rather than from physical overlap alone.

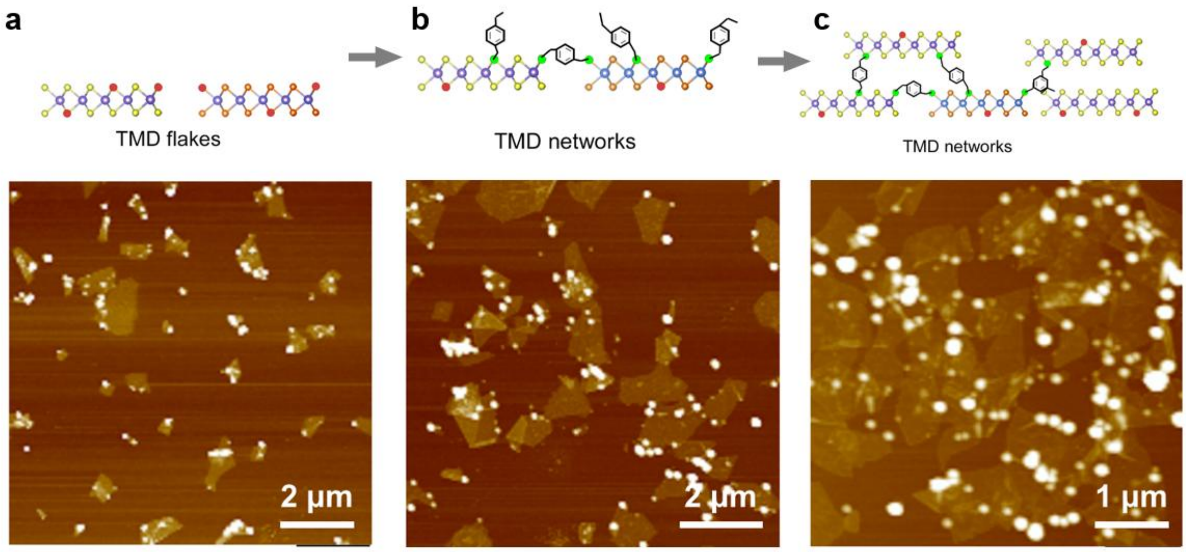

Figure 2. Formation of molecularly interconnected TMD nanosheet assemblies by alternating deposition and molecular functionalization. (a) Initial nanosheet assembly. (b) Molecularly connected assembly after a functionalization/deposition step. (c) More densely interconnected assembly obtained after further alternating processing. Each panel combines a schematic representation with the corresponding AFM image.

At the flake level, BDT acts as a bidentate linker because its two terminal thiols can participate in bond formation at chalcogen-deficient sites on different nanosheets. At the film level, repetition of this local connection generates a continuous molecularly coupled network. This multiscale relationship links the discrete-assembly objective of WP2 directly to the transport properties of later printed networks.

3.1.3 Electrical characterization

Electrical measurements were used as a functional test of whether the molecular treatment modifies interflake transport. Figure 3a shows the device-level functionalization scheme. The output characteristics in Figure 3b compare pristine TMD, annealed TMDs and BDT-functionalized TMD films, while Figure 3c shows the corresponding FET transfer characteristics. The BDT-treated films exhibit a markedly higher current than the pristine material, consistent with the improved interflake connectivity reported after molecular linking.

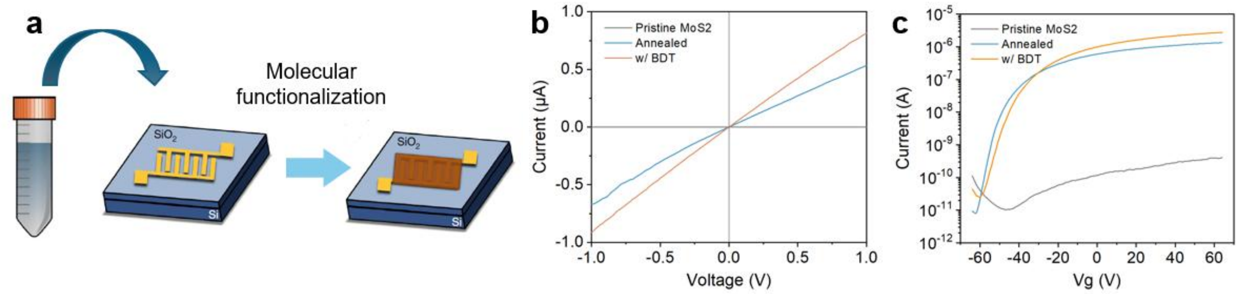

Figure 3. Electrical response of liquid-processed TMD networks after molecular functionalization. (a) Schematic of the functionalization of a deposited MoS_2. (b) Output characteristics of pristine, annealed and BDT-functionalized MoS_2 films. (c) Transfer characteristics of the corresponding FETs.

These results are consistent with the established role of conjugated dithiols in creating additional electronic pathways between solution-processed TMD flakes described in previous Deliverable reports.

3.1.4 Photoresponsive TMD films

Beyond using molecular chemistry to improve interflake coupling, the interconnected TMD platform was further post-functionalized with photoswitchable molecules. This additional molecular treatment is distinct from the bidentate-linking step itself: the linker establishes the interconnected nanosheet assembly, whereas the photoswitchable component introduces an optically addressable functionality. The molecules were selected according to their chemical compatibility with the TMD network and their relative energy alignment with the semiconductor.

The resulting device architecture is illustrated in Figure 4a. The output characteristics measured for the functionalized network in dark and under 365 nm and 530 nm illumination (Figure 4b) show a wavelength-dependent modulation of the current. The corresponding transfer characteristics (Figure 4c) display the same illumination-dependent response over the gate-voltage range. These measurements demonstrate that photoresponsive molecular functionality can be introduced into the molecularly engineered TMD network while retaining transistor operation.

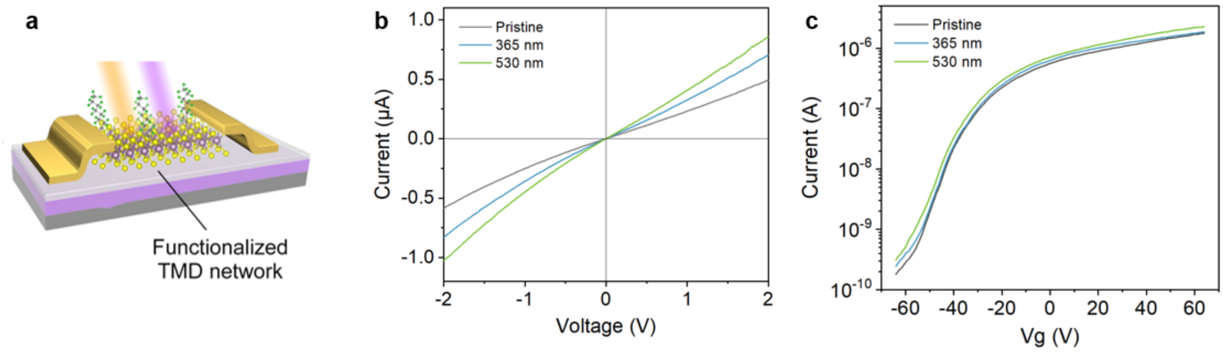

Figure 4. Photoresponsive optoelectronic device based on a molecularly functionalized TMD network. (a) Schematic of the device architecture containing the functionalized TMD network. (b) Output characteristics measured in dark (Pristine) and under 365 nm and 530 nm illumination. (c) Transfer characteristics measured under the same conditions.

The available measurements establish an illumination-dependent electrical response under UV and visible excitation. They do not, however, resolve the microscopic switching mechanism, switching kinetics, cycling endurance or long-term reversibility; these aspects are therefore not inferred in this deliverable.

3.2 Contribution to project (linked) Objectives

The work reported in D2.4 contributes to all three objectives of WP2. It advances O2.1 by exploiting chalcogen-defect sites for targeted molecular functionalization of solution-processed TMD nanosheets and by assessing the resulting changes in their spectroscopic and electronic properties. It contributes to O2.2 by establishing thiol-based anchoring chemistry as a functionalization strategy applicable to chemically distinct TMDs, including MoS_2 and WSe_2. Most directly, it addresses O2.3 through the use of bifunctional molecular linkers to create chemically defined connections between individual nanosheets. Repetition of this flake-level linking motif during deposition produces extended interconnected networks, thereby validating the chemical-coupling strategy required for the controlled linkage of nanosheets and providing a basis for the formation of flake-level heterostructures with well-defined molecular interfaces.

3.3 Contribution to major project exploitable result

This demonstrator directly supports Tasks 2.4 and 3.6. Furthermore, the findings of this study are interconnected with different deliverables, such as D3.5, and serve as core pillars for subsequent works related to devices relevant to WP6.

4 Conclusion and Recommendation

D2.4 establishes a molecular route for assembling discrete solution-processed 2DM nanosheets into chemically connected structures. BDT serves as a representative bidentate linker, exploiting thiol chemistry at chalcogen-deficient sites to combine defect functionalization with interflake coupling. Spectroscopic characterization confirms the applicability of this strategy to MoS_2 and WSe_2, AFM follows the evolution from dispersed flakes to interconnected assemblies, and electrical measurements show improved transport after BDT treatment. In addition, post-functionalization with photoswitchable molecules produced wavelength-dependent electrical responses under 365 and 530 nm illumination, showing that the interconnected assembly can host an additional optoelectronic function.

5 Risks and interconnections

5.1 Risks/problems encountered

Risk No.	What is the risk	Probability of risk occurrence[1]	Effect of risk[1]	Solutions to overcome the risk
7	Agglomerates of flake-level heterostructures are too big for direct printing: (i) M, (ii) L	2	3	Changed deposition technique to achieve a more uniform coating

1) Probability risk will occur: 1 = high, 2 = medium, 3 = Low

5.2 Interconnections with other deliverables

The flake-level molecular coupling strategy developed in D2.4 provides input for downstream activities on printed 2DM networks, multiscale characterization and electronic/optoelectronic devices. In these later activities, the linker-defined junction becomes a repeated element of the collective film and can be evaluated through network transport and device performance.

6 Deviations from Annex 1

Not applicable

7 Acknowledgement

The author(s) would like to thank the partners in the project for their valuable comments on previous drafts and for performing the review.

Project partners:

#	Partner short name	Partner Full Name
1	TCD	TCD THE PROVOST, FELLOWS, FOUNDATION SCHOLARS & THE OTHER MEMBERS OF BOARD, OF THE COLLEGE OF THE HOLY & UNDIVIDED TRINITY OF QUEEN ELIZABETH NEAR DUBLIN
2	UNISTRA	UNIVERSITE DE STRASBOURG
3	UKa	UNIVERSITAET KASSEL
4	BED	BEDIMENSIONAL SPA
5	TUD	TECHNISCHE UNIVERSITAET DRESDEN
6	VSCHT	VYSOKA SKOLA CHEMICKO-TECHNOLOGICKA V PRAZE
7	UNR	UNIRESEARCH BV
8	UniBw M	UNIVERSITAET DER BUNDESWEHR MUENCHEN
9	EPFL	ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE

Disclaimer/ Acknowledgment

This project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101135196. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

8 Appendix A - Quality Assurance Review Form

The following questions should be answered by all reviewers (WP Leader, reviewer, Project Coordinator) as part of the Quality Assurance procedure. Questions answered with NO should be motivated. The deliverable author will update the draft based on the comments. When all reviewers have answered all questions with YES, only then can the Deliverable be submitted to the EC.

NOTE: This Quality Assurance form will be removed from Deliverables with dissemination level "Public" before publication.

Question	**WP Leader**	**Reviewer**	**Project Coordinator**
	P. Samorì (UNISTRA)	G. S. Duesberg	Jonathan Coleman (TCD)
1. *Do you accept this Deliverable as it is?*	Yes	Yes	Yes
2. *Is the Deliverable complete?* - *All required chapters?* - *Use of relevant templates?*	Yes	Yes	Yes
3. *Does the Deliverable correspond to the DoA?* - *All relevant actions preformed and reported?*	Yes	Yes	Yes
4. *Is the Deliverable in line with the 2D-PRINTABLE objectives?* - *WP objectives* - *Task Objectives*	Yes	Yes	Yes
5. *Is the technical quality sufficient?* - *Inputs and assumptions correct/clear?* - *Data, calculations, and motivations correct/clear?* - *Outputs and conclusions correct/clear?*	Yes	Yes	Yes
6. *Is created and potential IP identified and are protection measures in place?*	No potential IP was identified by partners	No potential IP was identified by partners	No potential IP was identified by partners
7. *Is the Risk Procedure followed and reported?*	Yes	Yes	Yes
8. *Is the reporting quality sufficient?* - *Clear language* - *Clear argumentation* - *Consistency* - *Structure*	Yes	Yes	Yes