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

D3.5. – Second generation of printed network heterostructures: Use of bi- or multidentate molecular linkers to form conformal junctions.

Funded by
the European Union

Deliverable No.	D3.5	
Related WP	WP 3	
Deliverable Title	Second generation of printed network heterostructures: Use of bi- or multidentate molecular linkers to form conformal junctions.	
Deliverable Date	Sept 2026	
Deliverable Type	REPORT	
Dissemination level	Public (PU)	
Author(s)	JN Coleman (TCD) P Samori (UNISTRA)	2026-07-05
Checked by	Jonathan Coleman (TCD)	2026-07-05
Reviewed by	P Samori (UNISTRA) Francesco Bonaccorso (BeD)	2026-08-05
Approved by	Jonathan Coleman (TCD) - Project Coordinator	2026-08-05
Status	Final	2026-08-07

Document History

Version	Date	Editing done by	Remarks
V1.0	2026-08-07	Jonathan Coleman	

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

This deliverable reports the development of second-generation printed network heterostructures based on covalent cross-linking of nanosheets using bi- and multidentate molecular linkers. The objective is to reduce inter-nanosheet junction resistance by forming conformal plane-to-plane junctions, thereby improving charge transport in printed networks.

Liquid-phase exfoliated MoS_2 and graphene nanosheets were functionalized and chemically linked via diazonium-derived molecular bridges to form hybrid “super-dyad” structures. These hybrid materials were processed into inks and investigated using terahertz (THz) and transient absorption spectroscopy.

The results confirm successful covalent coupling and increased carrier density upon functionalization. However, spectroscopic analysis indicates limited evidence for efficient inter-nanosheet charge transfer. These findings provide important insight into the role of molecular linkers in nanosheet coupling and establish a foundation for further optimization of chemically cross-linked printed heterostructures.

Contents

List of Figures

List of Tables

No table entries found.

Abbreviations & Definitions

Abbreviation	Explanation
MoS_2	Molybdenum disulfide
THz	Terahertz
f-graphene	Functionalized graphene
f-MoS_2	Functionalized molybdenum disulfide

1 Introduction

Printed networks of solution-processed nanosheets represent a key materials platform for the development of large-area, low-cost electronic devices. However, electrical transport in such networks is typically limited by inter-nanosheet junctions, which introduce significant resistance and reduce the overall network mobility relative to the intrinsic properties of the constituent nanosheets. Reducing this junction resistance is therefore a central challenge in the development of high-performance printed electronics.

Within the 2D-PRINTABLE project, one of the primary strategies to address this limitation is the development of methods to strongly couple nanosheets through chemical functionalization and controlled junction engineering. In particular, the use of bi- or multidentate molecular linkers offers a route to forming covalent connections between nanosheets, enabling the formation of conformal, plane-to-plane junctions that may facilitate improved charge transfer across the network.

This deliverable describes the development of such second-generation heterostructures based on covalently linked nanosheets, as discussed in deliverables D3.2 and D3.3. Building on previous work on edge-to-edge junction formation, the present approach focuses on creating molecule-mediated plane-to-plane junctions between nanosheets, with the aim of enhancing interfacial electronic coupling. Graphene and MoS_2 were selected as model systems to form asymmetric hybrid structures, allowing the investigation of interfacial charge transfer processes in chemically linked two-dimensional materials.

2 Methods and core part of the report

2.1 Background

The performance of printed nanosheet networks depends critically on the nature of the junctions formed between individual flakes. In conventional networks, these junctions are typically governed by weak van der Waals interactions, leading to high junction resistance and limited charge transport. Chemical cross-linking using conjugated molecular linkers provides a promising strategy to overcome this limitation by introducing covalent bonding and enhancing electronic coupling between nanosheets.

In this work, we explore this concept using graphene and MoS_2 nanosheets linked via diazonium-based chemistry. The resulting hybrid structures are designed to form well-defined interfaces that enable investigation of through-molecule charge transfer and the extent to which molecular bridges can improve inter-nanosheet transport.

2.2 Procedures

Liquid-phase exfoliation was used to prepare dispersions of MoS_2 and graphene nanosheets. MoS_2 was exfoliated in dry acetonitrile at a concentration of 0.2 mg mL^{-1}, yielding flakes with lateral dimensions in the range 0.1 to 1 μm^2 and thicknesses between 3 and 10 nm. Graphene was exfoliated in Milli-Q water at a concentration of 0.8 mg mL^{-1}, producing flakes with lateral sizes between 0.5 and 6 μm^2 and thicknesses of 1 to 2.4 nm.

Following exfoliation, MoS_2 nanosheets were functionalized using N-(4-diazophenyl)maleimide to introduce reactive groups capable of forming covalent bonds. The functionalization process was followed by purification steps, including centrifugation and filtration, to remove unreacted species and impurities.

Hybrid structures were subsequently formed by combining functionalized MoS_2 (f-MoS_2) with graphene dispersions at different weight ratios. A representative synthesis involved mixing 27 mg of f-MoS_2 with 9 mg of graphene, corresponding to a 3:1 ratio. The mixture was filtered and redispersed in water to produce a stable hybrid ink suitable for further processing. The formation of covalently linked graphene–MoS_2 structures is illustrated schematically in Figure 1a.

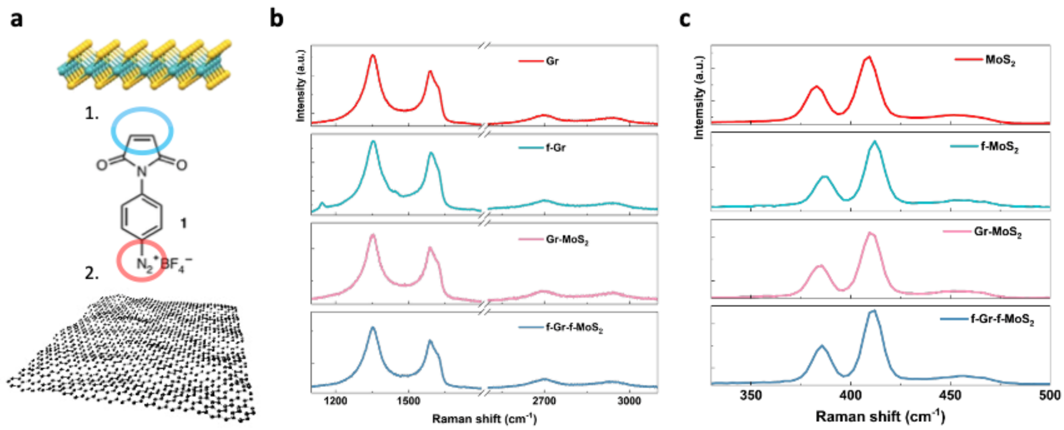


Figure 1. Covalently linked graphene-MoS_2. (a) Schematical representation of the multistep reaction yielding covalently linked graphene-MoS_2. The steps include: 1. Functionalization of liquid exfoliation

MoS_2 with N-(4-diazophenyl)maleimide; 2. Bridge formation using different f-MoS_2-graphene ratios. Raman spectroscopy comparison of characteristic (b) MoS_2 and (c) graphene bands for the pristine and functionalized architectures.

2.3 Data Analysis

Raman spectroscopy analysis was carried out to investigate preliminary interlayer interactions upon the formation of covalently linked architectures. The electronic properties of the hybrid materials were investigated using terahertz (THz) spectroscopy and transient absorption spectroscopy. THz measurements were used to probe photoconductivity and carrier dynamics, while transient absorption spectroscopy provided insight into excited-state behaviour and possible charge transfer processes. Data analysis was performed using OriginLab software.

3 Results & Discussion

3.1 Results

The synthesized material consists of covalently linked graphene–MoS_2 heterostructures in which individual nanosheets are connected via molecular bridges, forming asymmetric "super-dyad" structures. Raman spectroscopy was performed to analyze the characteristic vibrational bands of both MoS_2 and graphene. No significant changes were observed in the Raman spectrum of graphene after stacking with MoS_2 (Figure 1b). In contrast, the Raman bands of MoS_2 exhibited a shift toward lower wavenumbers following heterostructure formation (Figure 1c), indicating a modification of its lattice environment due to interaction with graphene. This architecture is designed to promote interfacial electronic coupling and enable charge transfer between the two materials.

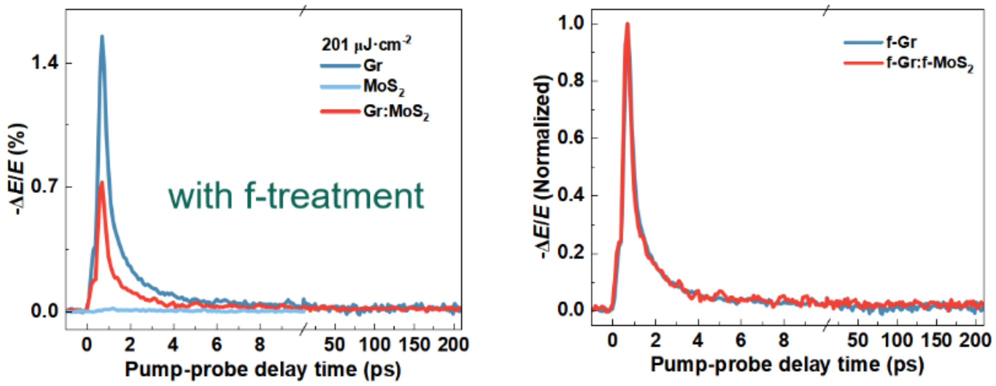


Figure 2. Transient absorption measurements of graphene, MoS_2 and the cross-linked graphene-MoS_2 hybrid. Left: absolute values, Right: normalized.

THz photoconductivity measurements were performed under different excitation conditions. Under below-bandgap excitation at approximately 1310 nm, no significant differences were observed in the carrier dynamics between graphene and the hybrid systems. However, the photoconductivity amplitude in the hybrid structures was reduced by approximately a factor of two compared to graphene alone, as shown in Figure 2. This reduction may be attributed to decreased carrier mobility arising from functionalization or increased scattering at the modified interfaces.

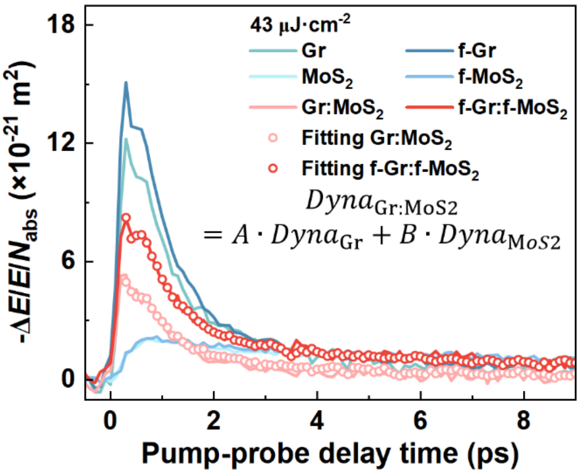
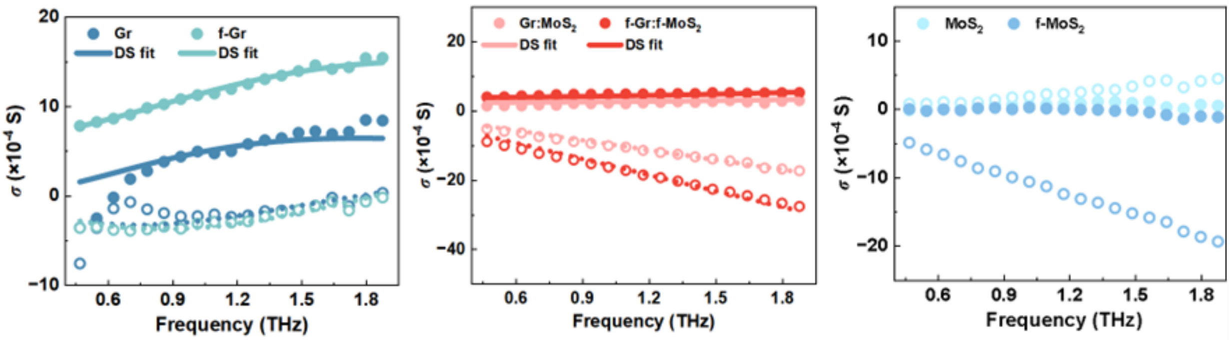


Figure 3. Graph showing that the hybrid TA spectrum is a linear combination of the individual components.

Under above-bandgap excitation, transient absorption measurements showed that the response of the hybrid system could be reproduced as a linear combination of the individual graphene and MoS_2 components, as illustrated in Figure 3. This observation suggests that any charge transfer occurring between the nanosheets is weak and does not significantly alter the overall excited-state dynamics. Further THz spectroscopy measurements, presented in Figure 4, indicate that functionalization leads to an increase in charge carrier density in both individual nanosheets and hybrid systems. This results in enhanced THz absorption and increased real conductivity under dark conditions. While this demonstrates that chemical modification can influence electronic properties, it does not provide direct evidence of efficient inter-nanosheet charge transfer.



	ω_P (THz)	τ_{DS} (fs)	c
Gr	402	90.2 ± 8.8	-1
f-Gr	716	65.3 ± 4.5	-0.78
Gr:MoS_2	1.7	2.3 ± 0.6	-0.99
f-Gr:f-MoS_2	2.2		

Figure 4. THz spectroscopy results for graphene and f-graphene as well as graphene/MoS_2 mixtures and functionalized f-graphene/MoS_2 hybrids.

Overall, the spectroscopic results indicate that although covalent linking between nanosheets is successfully achieved, the resulting electronic coupling is insufficient to produce strong or long-lived charge transfer under the conditions studied.

3.2 Contribution to project (linked) Objectives

The work presented in this deliverable contributes to the objectives of the 2D-PRINTABLE project by demonstrating a chemical strategy for forming strongly coupled nanosheet heterostructures. In particular, it addresses the development of methods to engineer inter-nanosheet junctions through covalent functionalization, with the aim of reducing junction resistance and improving network performance.

This work supports the objectives of WP3 related to the fabrication and optimization of printed networks and heterostructures, and contributes to the broader project goal of achieving nanosheet networks in which inter-flake transport approaches intrinsic material behaviour.

3.3 Contribution to major project exploitable result

This deliverable contributes to the development of scalable approaches for the fabrication of chemically engineered nanosheet networks. The demonstrated ability to form covalently linked graphene–MoS_2 heterostructures provides a platform for further exploration of molecular linker strategies and their impact on electronic properties.

The findings also identify key limitations of the current approach, particularly in relation to achieving efficient charge transfer across molecular junctions, thereby guiding future efforts toward improved linker design and device integration. In future, further set of multifunctional molecules can be explored.

4 Conclusion and Recommendation

In this deliverable, covalently linked graphene–MoS_2 hybrid nanosheet systems have been successfully synthesized using diazonium-based molecular linkers. The formation of these heterostructures demonstrates the feasibility of creating conformal, molecule-mediated junctions between nanosheets. Spectroscopic analysis shows that functionalization increases carrier density and conductivity, but provides limited evidence for efficient inter-nanosheet charge transfer. These results indicate that while chemical cross-linking is a viable strategy for nanosheet coupling, further optimization is required to achieve the level of electronic interaction needed to significantly enhance network transport properties.

Future work should focus on the design of more effective molecular linkers with improved electronic coupling, as well as device-level measurements to directly assess transport across junctions. Advanced spectroscopic techniques may also provide further insight into the dynamics of charge transfer in these systems.

5 Risks and interconnections

5.1 Risks/problems encountered

The main limitation encountered in this work is the lack of clear evidence for efficient charge transfer between covalently linked nanosheets. In addition, distinguishing between intra-flake and inter-flake transport contributions in spectroscopic measurements remains challenging.

5.2 Interconnections with other deliverables

This work is closely linked to activities in WP2 related to nanosheet functionalization and to WP5 and WP6, where the electrical properties of nanosheet networks and devices are evaluated. The materials developed here provide a basis for future integration into printed electronic devices.

6 Deviations from Annex 1

No significant deviations from Annex 1 were identified. The objectives of developing chemically coupled nanosheet heterostructures have been achieved.

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.

7 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**
	Jonathan Coleman (TCD)	Francessco Bonaccorso (BeD)	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?*	Yes	Yes	Yes
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