Publishable Summary for 20FUN03 COMET
Two dimensional lattices of covalent- and metal-organic frameworks for the Quantum Hall resistance standard

Overview
Graphene's electrical properties have widespread potential, but the adoption of graphene´s Quantum Hall Resistance Standard (QHRS) in metrology, and by industrial end-users, is currently limited by the inability to grow large areas of high-quality graphene. To alleviate these issues, this project will assess and benchmark a new family of graphene-like analogues for realising the QHRS: two-dimensional lattices of covalent- and metal-organic frameworks. These novel materials will be defined in an atomically precise and scalable manner, so that they may eventually replace graphene in metrology and other sectors where the "uniqueness" of graphene properties is exploited.

Need
The European Commission has identified graphene and 2D materials as key emerging technologies with transformative potential for industry. The global market for graphene alone, is estimated in ~370 million € by 2024. Within this context, the Graphene Flagship aims to bring graphene innovation from the laboratory to commercial applications.

Regarding metrology, a wide dissemination of the International System of Units outside metrology institutes requires a simpler implementation of quantum standards. The recent development of graphene-based quantum Hall resistance standard (QHRS) partially addresses this need. Exploiting the novel physical properties of graphene's band diagram, graphene-based QHRS demonstrated superior performance (less demanding measurement conditions) than traditional approaches.

However, whilst graphene is a good candidate for QHRS, its electronic properties are known to strongly depend on sample preparation history and the nature of the substrate onto which is deposited. Furthermore, the inability to grow large areas of graphene with controlled and stable doping limits its widespread adoption in electronic industry and in metrology. High-quality 2D materials suitable for optoelectronic devices with large functional areas and high uniformity are needed.

This project aims tackling these challenges through the development, characterisation and benchmarking of novel Dirac-like materials based on two-dimensional covalent- and metal-organic frameworks (2D-COF/MOFs). These materials are unique because their chemistry, morphology and electronic properties can be finely tuned in an atomically precise and scalable manner.

The project will be the first international coordinated research effort towards a metrological application of electronic devices based on these novel materials, and will underpin European leadership in this new field of science. The project will have a positive impact beyond the immediate metrological benefits to various emerging technologies, including solar energy conversion, sensing, membranes, optoelectronics and spintronics, and new lines of materials research.

Objectives
The overall objective of the project will be to assess (benchmark) the potential of 2D organic- and metal-organic frameworks for realising the QHRS. The specific objectives of the project are:

1. **To develop single layered two-dimensional Dirac covalent- and metal- organic frameworks** (**2D-COF/MOFs)** in which graphene-like hexagonal structures are obtained from trigonal organic ligands. The chemistry, morphology and electronic properties of 2D-COF/MOFs will be tuned in an atomically precise and scalable manner. Target values for doping and mobility respectively are: ~10^{10} cm^{-2} and μ > 10000 $cm^2V^{-1}s^{-1}$.
2. **To perform traceable multi-scale characterization on the 2D-COF/MOFs samples.** Specifically, to characterize their electrical properties as a function of sample's area and the nature of the employed substrate (prior to and after integration into QHRS devices).
3. **To perform QHE measurements on the manufactured devices and to assess the potential of 2D-COF/MOFs materials for realising the QHRS.** Specifically, to benchmark QHRS devices based on these samples vs those based on graphene and AlGaAs/GaAs hetero-structures, targeting B,T,I of <15 T, > 100 µA and/or >1.5 K, while preserving typical relative uncertainty within 10^{-9}.
4. **To assure European leadership on the research of novel class of 2D materials** by establishing the research capabilities, appropriate protocols, quality schemes and traceability and facilitate the take up of the technology and measurement infrastructure developed in the project by the metrology community and in the development of emerging technologies such as solar energy conversion, sensing, membranes, optoelectronics, spintronics, etc. **To disseminate the results to stakeholders** (within and beyond the metrology community) in order to enable research cooperation that can be sustained in the long term.

Progress beyond the state of the art
While many 2D materials have been introduced, graphene uniquely displays charge transport properties linked to massless charge carriers, due to its Dirac-like energy band diagram. So, developing novel Dirac materials with finely controlled doping represents a breakthrough in science and technology, allowing new Dirac materials with the advantages of graphene and without its limitations.

To date, most of 2D-COFs/MOFs single layer samples are flakes with diameters of few tens of nanometres, developed by mechanical exfoliation. Recently, synthesis approaches established by members of this consortium have allowed to develop single 2D-COF/MOFs layers at wafer relevant scales. These approaches are employed in COMET for the first time for the synthesis of novel Dirac materials.

This project uses improved synthesis methods to make large single layers of 2D MOF-COF novel materials easy to integrate in devices. Furthermore, doping control is addressed to metrology needs (carrier concentration~$10^{10}cm^{-2}$, with Fermi level right at the Dirac cone intersection).

The QHRS is usually realized from GaAs/AlGaAs-based QHE devices operating at high magnetic field (~10 T), low temperature (1.5 K) and low current (<100 µA), with typical relative uncertainty within 10^{-9}. QH devices based on epitaxial graphene grown on SiC have shown Hall quantization at identical uncertainty level in more relaxed conditions, down to 3.5 T, up to 10 K and up to 0.5 mA.

Within this project, the ability to control the doping of samples, specifically achieving very low values (~10^{10} cm^2), keeping spatial homogeneity and high mobility opens a way to realize the QHRS under very low magnetic fields (~1T), if the Landau gap in the energy band diagram is sufficiently large. Furthermore, these methods have potential to realize the Quantum Anomalous Hall effect (QAH); that is, quantized Hall resistance at zero magnetic field, allowing widespread dissemination of electrical metrology standards.

Results
To develop single layered two-dimensional Dirac covalent- and metal- organic frameworks (2D-COF/MOFs):

In this period the synthesis of samples has been done according to a Bottom-up approach.
TUD has initiated the synthesis of samples using several methods as the air-liquid interfacial synthesis. Samples of types BHT-Cu, BHT-Ni (benzene-based) and Cu-6F-6OH-cHBC 2D MOF's has been obtained. BHT-Cu samples with a Kagome lattice have been structurally characterized by several techniques (Raman, AFM, SAED, AC-HRTEM, GIXRD). The samples consist on large area (cm^2) films which are polycrystalline at the monolayer level, a monolayer with a thickness of 0,74 nm. After that, the BHT-Cu monolayers were coupled

with large-area chemical vapor deposited (CVD) graphene using a wet transfer technique to produce a cm^2-scale 2D van der Waals heterostructure (vdWh). Also, synthesis of P2TANG polymer by Chemical Vapour Deposition (CVD) method has been initiated in TUD. The synthesis of TBTANG monomer, which is required for the synthesis of P2TANG polymer, was carried out at TUBITAK. The Raman spectrum shows different signals after a CVD process. Structural characterization has been performed as a function of temperature. Scaling the samples is challenging and strongly dependent on the employed substrate.

Using the technique SR-ARPES, IMDEA-Nanociencia has already been able to resolve the electronic structure of 2D systems as single layer of transition metal-dichalcogenides grown onto graphene, as well as graphene heterostructures, resolving Dirac cones and band gap opening engineering in graphene heterostructures. Besides, IMDEA is able to transfer samples from STM to ARPES chamber without breaking the ultra-high vacuum conditions. Thus, it’s possible to correlate the structural characterization with electronic band structure of the resulting proposed samples. In conjunction with TUD, HZDR has characterized the materials using computer simulations based on DFT and DFTB methods. In particular BHT-Cu and Cu-6F-6OH-cHBC 2D MOF’s structures have been predicted as a reference for experimental characterization, as well as their electronic band structures and carrier mobilities. BHT-Cu proved out to be a metallic material without Dirac properties, which also translates to its heterostructure with graphene, which was synthesized by TUD. Cu-cHBC MOF proved to be a semiconducting material with typical kagome lattice band structure and potentially interesting topological properties, which are still being evaluated.

Besides, TUD has develop an on-liquid-gallium surface synthesis (OLGSS) strategy under CVD conditions for the controlled growth of BHT-Cu thin films with ten-fold improvement of surface flatness (surface roughness can reach as low as ~2 Å) compared with MOF films grown by the traditional methods. The resultant ultra-smooth BHT-Cu films enable the formation of high-quality electrical contacts with gold (Au) electrodes, leading to a reduction of contact resistance by over ten orders of magnitude compared to the traditional uneven MOF films. Furthermore, due to the efficient interfacial interaction benifited from the high-quality contacts, the prepared BHT-Cu/MoS_2 vdWh exhibits intriguing photoluminescence (PL) enhancement, PL peak shift and large work function modulation.

To perform traceable multi-scale characterization on the 2D-COF/MOFs samples:

TUD and IMDEA-Nano performed a preliminary characterization on the interlayer coupling between BHT-Cu and graphene layers. Raman and terahertz time-domain spectroscopy (THz-TDS) studies, combined with electrical measurements and theoretical modeling, demonstrate significant hole transfer from monolayer BHT-Cu to graphene upon contact, leading to a downshift of the Fermi level in graphene arising from the strong interlayer electronic coupling. Furthermore, time-resolved THz spectroscopy (TRTS) reveals highly efficient photoinduced electron transfer from BHT-Cu to graphene (up to 34%), surpassing those of graphene-based bilayer vdWhs (up to 10%) quantified by the same technique.

The nanofabrication team at IMDEA-Nano worked on fabricating the Hall bar devices for the electrical characterisation of samples BHT-Cu. 6 samples were sent to TUD, 2x Silicon substrates, 2x SiOx/Si substrates and 2x SiOx/Si substrates with pre-patterned CrAu markers. Monolayer samples of BHT-Cu were deposited by TUD onto the surface of the substrates and sent back to IMDEA-Nano. The preliminary characterisation was performed employing optical, AFM and electronic microscopy. The images obtained were used to define the Hall bars via correlative UV laser mask less lithography onto negative tone resist. After this step, a reactive ion etching with CF4/Ar/O2 gas was used to remove the unwanted MOF material. Then, a second lithography step was performed to define the contact geometry, followed by a TiAu metal evaporation and lift-off process. Two samples were manufactured containing 6x hall-bar devices with manufacturing yield of >90%.

INRIM has implemented an ERT (Electrical Resistance Tomography) setup for measurements on up to 16 contacts. Measurements on both unpackaged samples (1 cm^2 samples with a fixture with spring contacts) and packaged ones can be performed. The reconstruction software, based on the EIDORS open source package, is operative. Test measurements on structured thin films were performed.

POLITO and INRIM implemented and tested a correlation noise spectrometer working in the 10 mHz-10 kHz frequency range, for four-terminal measurements on thin films. The analogue front-end is composed of commercial low noise voltage amplifiers; the digitizing is performed by an NI PXI board. A low-noise bias circuit for the samples has been designed and implemented. With this setup, POLITO and INRIM performed measurements of electrical noise on three samples (graphene, graphene/MOF, MOF/graphene/MOF) from batch 1.0. For these samples, INRIM and POLITO performed also measurements of contact resistance and material conductance.

CEM has completed the hardware to develop its ERT setup. Configuration of the equipment has been optimized. Also, several ghost samples to test the instrument have been built. Development of software is ongoing.

GUM implemented and tested a noise spectrometer based on a specially designed and prepared preamplifier cooperated with a commercial spectrum analyzer, for measurements of new 2D COF/MOF structures. Setup works in the frequency range from 10 kHz to 100 MHz. The work showed the possibility of reducing the noise figure (NF) by twenty times compared to the operation without a specially prepared preamplifier, whose task, apart from reducing noise, was to impedance match the measurement field with the analyzer input.

Electrical measurements have been performed on Hall bar devices based on BHT-Cu developed by TUD. 2-point current-voltage measurements indicate the MOF layers have very high resistivity. Some indication of electrical response to a gate voltage has been detected. Raman spectroscopy on the BHT-Cu Hall bars show no evidence of Raman modes associated to the MOF layer.

Time resolved THz spectroscopy was employed on BHT-Cu samples developed in A2.1.1. 2 and deposited on THz transparent fused silica substrates. The combination of low optical density and low doping*mobility product provided a null TRTS response in the samples – consistent with electrical characterization.

To perform QHE measurements on the manufactured devices and to assess the potential of 2D-COF/MOFs materials for realizing the QHRS.

The work on this objective has just begun due to the first batch of samples not showing the quantum Hall effect. New devices have been fabricated and distributed to the partners.

Impact

The dissemination of project results in media which is closely monitored by industry will ensure that the maximum benefits are achieved regarding early impact on industrial and other user communities, as well as the promotion of the resources and results of the project, be boosted by press releases and social media channels. Furthermore, specific training activities have been scheduled in order to foster and improve the understanding/collaboration between the metrology community and academia.

In this first period many talks were given at conferences targeting academic audiences. Also, several talks were given to public bodies or agencies. Also, the first international conference on organic 2D crystalline materials and devices was organized by members of the consortium (participation of >50 people from a dozen of countries).

Impact on industrial and other user communities

The developments planned in the project, such as band-structure engineering, doping control, stability, devices with good electrical contacts are basic requirements for application in electronics well beyond the development of electrical standards within metrology. The consortium will develop and adapt several tools within the project for electrical characterization aimed at supporting users from the semiconductor and electronics industry (e.g. the electrical resistance tomographer, correlation noise spectrometer). To promote this, video material on the use of specific techniques for precision resistance measurements in an industrial or academic research lab will be made available to stakeholders on the project website and promoted on the NMI partner's websites.

Furthermore, the know-how and related infrastructure required for 2D MOF/COF encapsulation and packaging will be developed within the project so that end users who lack resources such as techniques, instrumentation or sufficient expertise on the topic may benefit. This will be offered as a service to support industrial and/or academic end-users.

Impact on the metrology and scientific communities

The project will help emerging/smaller NMIs in the consortium to develop their capabilities in line with European NMI/DI levels. For example, training between metrological institutes e.g. in reference to the transfer of knowledge linked with the service for a portable modern cryogenic current comparator. Additionally, the project will foster direct interaction between NMIs and EU academic research institutions. This will increase recognition of the need for cross-disciplinary work, and promote the contribution of metrology with scientific communities and academia. This will be achieved via the academic partners and through various training materials aimed at universities and research laboratories produced during the project.

The novel material devices developed in the project to realise the QHRS under relaxed experimental conditions have potential for use in other metrology applications (e.g. for advanced impedance standards), as well as for potential applications in industrial calibration laboratories. Advanced QHRS may also have an impact on mass metrology with the redefinition of the kilogram being based on the Planck constant within the revised SI, and the Kibble balance experiment.

The large degree of in-plane tunability offered by 2D COF/MOF compounds is outstanding; novel graphene-like COF/MOF analogues will combine (i) 2D hexagonal lattices displaying programmed composition, structure and morphology, (ii) large specific surface area, (iii) ultra-high electron mobilities and (iv) an energy band diagram displaying Dirac cones. Such an endeavour will be instrumental towards the introduction of 2D COF/MOF compounds into the library of currently available inorganic 2D materials and their hetero-structures (with emerging and unique functionalities). As such, the potential impact and benefits of successfully addressing the proposed topic go well beyond metrology, with 2D materials and their hetero-structures being currently studied and applied in a plethora of emerging technologies linked with e.g. solar energy conversion, sensing, membranes, optoelectronics, spintronics, etc.

The project was mentioned in a media briefing by EURAMET titled "*EMPIR project develops a new method for Graphene characterisation*". Also more than thirty talks or posters in different conferences are related with the project. The project was explicitly presented in the poster titled "*EMPIR project COMET: Two dimensional lattices of covalent- and metal-organic frameworks for the Quantum Hall Resistance Standard*" at the Quantum 2021 Conference and in the talks "*Quantum-Based Resistance Metrology - Topical aspects of metrology and potential of new standards*" in the Topological Matter Conference 2021 and in the talk *"Proyecto 20FUN03 COMET. Nuevos materiales para la Resistencia Hall Cuántica"* (in Spanish) at the Seventh Spanish Congress of Metrology.

Impact on relevant standards

Early impact on SI measurement standards and on international documentary standards is expected by informing relevant metrology committees and standardization bodies of the project's progress in the new field of QHE physics in 2D COF/MOF.

Regarding the potential of such novel systems for future QHR standards for the SI ohm realization, the relevant committees are expected to be highly supportive of developing the technologies in this project, and will be kept informed of the progress. Participating institutes already have high-level metrological input into these metrology committees and so special attention and feedback will be given to areas where enhanced quantum resistance standards are most relevant. The consortium's membership of several standardisation and technical committees will ensure early impact of project results on the relevant standards documents. The project will be represented in key European and international committees related to electrical metrology, such as the EURAMET Technical Committee on Electricity and Magnetism (TC-EM) and the CCEM Working Group on Low-Frequency Quantities (WGLF).

The project will also be represented in several European and international pre-normalisation initiatives and standardisation bodies e.g. CEN/TC352, ISO/TC229 and IEC/TC113, regarding the 2D materials developed and the characterization protocols developed.

Longer-term economic, social and environmental impacts

Early impact on standards is expected by informing relevant standard committees and bodies of the project's progress in the new field of QHE physics in 2D COF/MOF. Regarding the potential of such novel systems for future QHR standards, the relevant committees are expected to be highly supportive of developing the technologies in this project, and will be kept informed of the progress. Participating institutes already have high-level metrological input into these standards bodies and so special attention and feedback will be given to areas where enhanced quantum resistance standards are most relevant. The consortium's membership of several standardisation and technical committees will ensure early impact of project results on the relevant standards documents.

List of publications

1. Lu, Y. et al (None) 'sp-Carbon Incorporated Conductive Metal-Organic Framework as Photocathode for Photoelectrochemical Hydrogen Generation', *Angewandte Chemie International Edition* 61(39) p. e202208163. Available at https://doi.org/10.1002/anie.202208163
2. Lu, Y. et al (None) 'Precise tuning of interlayer electronic coupling in layered conductive metal-organic frameworks', *Nature Communications* 13(1) p. 7240. Available at https://doi.org/10.1038/s41467-022-34820-6
3. Liu, K. et al (None) 'A Quasi-2D Polypyrrole Film with Band-Like Transport Behavior and High Charge-Carrier Mobility', *Advanced Materials* 35(40) p. 2303288. Available at https://doi.org/10.1002/adma.202303288
4. Parreiras, S.O et al (None) 'Lanthanide metal–organic network featuring strong perpendicular magnetic anisotropy', *Nanoscale* 15(16) p. 7267-7271. Available at https://doi.org/10.1039/D2NR07189D
5. Sporrer, L. et al (None) 'Near IR Bandgap Semiconducting 2D Conjugated Metal-Organic Framework with Rhombic Lattice and High Mobility', *Angewandte Chemie International Edition* 62(25) p. e202300186. Available at https://doi.org/10.1002/anie.202300186
6. Zhang, J. et al (None) 'Wavy Two-Dimensional Conjugated Metal–Organic Framework with Metallic Charge Transport', *Journal of the American Chemical Society* 145(43) p. 23630-23638. Available at https://doi.org/10.1021/jacs.3c07682
7. Wojciechowski, Marcin, Kateryna Hovorova, Kateryna (None) 'The development and tests of a preamplifier for the spectrum analyzer adopted for noise measurements in quantum Hall standard', *2023 IMEKO TC-4 International Symposium Proceedings* p. 27-31. Available at https://conferences.imeko.org/event/3/attachments/6/445/Proceedings2023%20IMEKO%20TC4.pdf

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link

Project start date and duration:	01 June 2021. 36 Months	
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