From solution to surface:
2*D*-organization of fluor*E*scent fun*C*tionality *O*n g*R*aphene b*A*sed ma*TE*rials

DECORATE

Partner 1 (Principal investigator)

Equipe Nanomatériaux et Matériaux Nanostructurés (NARCOS)
Dr. Imad ARFAOUI, imad.arfaoui@sorbonne-universite.fr , 01 44 27 26 96
Sorbonne Université, CNRS UMR 8233, MONARIS,
4 Place Jussieu, 75252 Paris Cedex 05, Paris.

Partner 2

Equipe Chimie des Polymères (ECP)
Dr. Lydia SOSA VARGAS, l.sosa-vargas@sorbonne-universite.fr, 01 44 27 55 85
Sorbonne Université, CNRS UMR 8232, Institut Parisien de Chimie Moléculaire,
4 Place Jussieu, 75252 Paris Cedex 05, Paris.

Partner 3

Surfaces and Thin Films group
Prof. Dr. Petra RUDOLF, p.rudolf@rug.nl, +(31)50-363 4736
University of Groningen, Zernike Institute for Advanced Materials,
Nijenborgh 4, 9747 AG Groningen, The Netherlands.

CV des porteurs de chaque équipe (1 page max/personne)/CV of the PIs of each partner

Partner 1: Imad ARFAOUI received his Ph.D. in Physics from Ecole Centrale Paris in 2001 (Title: Nanoscale study of niobium oxide films for the improvement of superconducting cavities used in particle accelerators) for his work in Surface Science at CEA Saclay. His research works are focused on elaboration and characterization of nanomaterials enabling him to acquire an expertise in Surface Science and scanning probe microscopies (STM and AFM).
From 2001 until 2004, he joined Physics Institute of Nanostructures at Ecole Polytechnique Fédérale de Lausanne (Switzerland) where he worked both on carbon nanotubes and thin oxide films. In 2004, he moved to the University of Groningen (The Netherlands) to participate to the creation of the Surfaces and Thin films group. Until 2007, he worked on synthesis and characterization of well-defined nanostructures encapsulated and stabilized within carbon-based materials, oxides and self-assembled organic thin films, and surface immobilization of functionalized colloidal nanoparticles. In 2007, in the Nanophotonics group at CEA Saclay (France), he studied some supramolecular architectures at the liquid-solid interface.
Since 2008, he is staff member of Laboratoire des Matériaux Mésoscopiques et Nanométriques, renamed MONARIS (De la Molécule aux Nano-objets : Réactivité, Interactions et Spectroscopies), as CNRS research engineer-physicist in charge of scanning probe microscopy facilities. He developed some deep investigations on the electronic and mechanical properties of colloidal crystals. Since few years, he is interested in the design and fabrication of functional, integrated nanostructures based on functional surface-confined 2D-assemblies. The latter are obtained from 3D-molecular building block based on phthalocyanine and porphyrin derivatives with varied design features.
He has co-authored of 36 peer-reviewed publications (h-index = 19) and in 2014 he received "Habilitation à Diriger des Recherches" diploma from Sorbonne Université.

5 selected publications

1***)*** **2D host-guest supramolecular chemistry for an on-monolayer graphene emitting platform**, B. Kim; C. Cho, **I. Arfaoui**, C. Paris, C. Petit, T. Le Bahers, E. Kim, A. J. Attias, *Materials Horizons* **2020**, 7 (10), 2741-2748.

2***)*** **Probing the in-air growth of large area of 3D functional structures into a 2D supramolecular nanoporous network**, R. Brisse, D. Guianvarc'h, C. Mansuy, S. Sagan, D. Kreher, **L. Sosa-Vargas**, L. Hamitouche, V. Humblot, **I. Arfaoui**, V. Labet, C. Paris, C. Petit, A. J. Attias, *Chemical Communications* **2018**, 54 (72), 10068-10071.

3***)*** **Star-shaped ethynylpyrimidine with long alkoxyl side chains: synthesis, fluorescence and 2D self-assembling**, S. Achelle, N. Ple, D. Kreher, A. J. Attias, **I. Arfaoui**, F. Charra, *Tetrahedron Letters* **2009**, 50 (50), 7055-7058.

4***)*** **Periodic Positioning of Multilayered 2.2 Paracyclophane-Based Nanopillars**, D. Bleger, D. Kreher, F. Mathevet, A. J. Attias, **I. Arfaoui**, G. Metge, L. Douillard, C. Fiorini-Debuisschert, F. Charra, *Angewandte Chemie, International Edition* **2008**, 47, 8412-8415.

5***)*** **Selective immobilization of nanoparticles on surfaces by molecular recognition using simple multiple H-bonding functionalities**, C. R. van den Brom, **I. Arfaoui**, T. Cren, B. Hessen, T. T. M. Palstra, J. T. M. De Hosson, **P. Rudolf**, *Advanced Functional Materials* **2007**, 17, 2045-2052.

Partner 2: Lydia SOSA VARGAS - CNRS tenured researcher working in the Paris Institute of Molecular Chemistry (IPCM) at Sorbonne University (SU). Research expertise encompasses synthetic organic chemistry, physical studies of organic dyes and semiconducting liquid crystalline materials, organic electronics and the study of molecular and nanoscale self-assembling materials for photonic and plasmonic applications.

RESEARCH EXPERIENCE

2017 - now **CNRS researcher**, IPCM-Equipe Chimie des Polymères, SU, Paris, France.
2015 - 2017 **Postdoctoral researcher**, ECP-IPCM, SU, Paris, France.
2012 - 2015 **Postdoctoral researcher**, National Institute of Advanced Industrial Science & Technology (AIST-Kansai), Japan.
2011 - 2012 **Postdoctoral researcher** (part-time) University of East Anglia, Norwich, UK.
2006 - 2007 **Project Scientist**, York University, Toronto, Canada.

EDUCATION

2012 - PhD in Synthetic Organic Chemistry, University of East Anglia, UK.

AWARDS & SCHOLARSHIPS

2017 ***'300 talents 2017'*** *L'Oréal-UNESCO For Women and Science Program*, France
2016 Nomination for the **67th Lindau Nobel Laureate Meeting**, CNRS France
2016 ***SNI-member Level 1*** (National Mexican System of Researchers) –Mexican Council of Science & Technology (CONACYT), Mexico
2014 ***Iris/Kousai award*** *for young researchers*, Japanese Liquid Crystal Society, Japan
2007 **CONACYT Postgraduate Scholarship***,*

5 selected publications

1*)* Probing the in-air growth of large area of 3D functional structures into a 2D supramoleculakr nanoporous network*,*** R. Brisse, D. Guianvarc'h, C. Mansuy, S. Sagan, D. Kreher, **L. Sosa-Vargas**, L. Hamitouche, V. Humblot, **I. Arfaoui**, V. Labet, C. Paris, C. Petit, A.-J. Attias, *Chem. Comm.* **2018**, Advance article.

2) **Beyond "decorative" 2D-supramolecular self assembly; a new strategy towards functional surfaces for nanomaterials**, **L. Sosa-Vargas**, E. Kim, A.-J. Attias, *Mater. Horiz,* **2017**, *4*, 570-583.

3) **Ordinary and Hot Electroluminescence from Single-Molecule Devices: Controlling the Emission Color by Chemical Engineering**, Michael C. Chong,* **L. Sosa-Vargas**,* H. Bulou, A. Boeglin, F. Scheurer, F. Mathevet, G. Schull, *Nano Lett*., **2016**, *16* (10), pp 6480–6484. (*equal contribution)

4) Discotic liquid crystal functionalized gold nanorods: 2- and 3D self-assembly and macroscopic alignment as well as increased charge carrier mobility in hexagonal columnar liquid crystal hosts affected by molecular packing and π- π interactions, X. Feng, **L. Sosa-Vargas**, S. Umadevi, T. Mori, Y. Shimizu and T. Hegmann, *Adv. Funct. Mater.* **2015**, *8*, 116.

5) Synthesis and Properties of the Hybrid Phthalocyanine-Tetrabenzoporphyrin Macrocycles A. N. Cammidge, I. Chambrier, M. J. Cook and **L. Sosa-Vargas**, *Handbook of Porphyrin Science* Vol. 16, **2012**, K. M. Kadish, K. M. Smith, R. Guilard (Eds.) World Scientific, 331-404.

Partner 3: Petra RUDOLF is Professor of Experimental Solid State Physics and Head of the Surfaces and Thin Films department of the Zernike Institute for Advanced Materials at the University of Groningen.

Education
1995 Doctorat en Sciences - groupe des Sciences Physiques [PhD in physics] plus grande distinction avec félicitations du jury (summa cum laude), supervisor: Prof. Roland Caudano, University of Namur, Belgium Thesis title: "Structural, vibrational and electronic properties of ultrathin C60 films on metallic substrates".
1987 Laurea in Fisica [equivalent to MSc in Physics] 110/110 con lode (summa cum laude), supervisor: Prof. Andrea Frova, Università degli Studi di Roma "La Sapienza", Rome, Italy, Thesis title: "Silicio amorfo idrogenato depositato mediante fasci ionici" (Hydrogenated amorphous silicon deposited by ion beams).

Recent Professional Positions
Feb/20 – present: Dean of Graduate Studies at University of Groningen (2x2 year mandate half time, in addition to the academic tasks & heading the Surfaces and Thin Films group at the Zernike Institute for Advanced Materials); 2014-2018: Director of the Graduate School of Science and Engineering at the University of Groningen (4-year mandate full time); 2003-2014 Full Professor and since 2014 Senior Full Professor of Experimental Solid State Physics at the Zernike Institute for Advanced Materials, University of Groningen, The Netherlands (tenure position); 2003-08: Editor-in-Chief of the European Physical Journal B (part-time in addition to teaching and research duties at the University of Groningen)

Research Interests
Her principal research interests lie in the areas of condensed matter physics and surface science, particularly molecular motors, 2D solids, organic thin films and inorganic-organic hybrids.

Publications: >270 peer-reviewed research publications and >32 book chapters (> 9.000 citations and h-index 51 Web of Science; > 11.800 citations h-index 57 Google Scholar)
Colloquia & Seminars/Invited Talks at Nat. and Int. Conferences: 122/103 (of which 13 plenary).

Students/Postdocs advised: Prof. Rudolf advised 23 postdoctoral researchers; 29 PhD students

5 selected publications

1*)* **Top-down and bottom-up approaches to transparent, flexible and luminescent nitrogen-doped carbon nanodot-clay hybrid films**, Dimos, K.; Arcudi, F.; Kouloumpis, A.; Koutselas, I. B.; **Rudolf, P.**; Gournis, D.; Prato, M., *Nanoscale* **2017**, *9* (29), *10256-10262.*

2*)* **Comparing Graphene Growth on Cu(111) versus Oxidized Cu(111)**, Gottardi, S.; Muller, K.; Bignardi, L.; Moreno-Lopez, J. C.; Pham, T. A.; Ivashenko, O.; Yablonskikh, M.; Barinov, A.; Bjork, J.; **Rudolf, P.**; et al., *Nano Letters* **2015**, *15* (2), 917-922

3*)* **Design of molecule-based magnetic conductors**, Akhtar, N.; Blake, G. R.; Felici, R.; Amenitsch, H.; Palstra, T. T. M.; **Rudolf, P.**, *Nano Research* **2014**, *7* (12), 1832-1842

4*)* **One-Pot Functionalization of Graphene with Porphyrin through Cycloaddition Reactions**, Zhang, X. Y.; Hou, L. L.; Cnossen, A.; Coleman, A. C.; Ivashenko, O.; **Rudolf, P.**; van Wees, B. J.; Browne, W. R.; Feringa, B. L., *Chemistry-a European Journal* **2011**, *17* (32), 8957-8964.

5*)* **Functionalization of Graphene via 1,3-Dipolar Cycloaddition**, Quintana, M.; Spyrou, K.; Grzelczak, M.; Browne, W. R.; **Rudolf, P.**; Prato, M., ACS Nano **2010**, *4* (6), 3527-3533.

Résumé du projet/Summary of the project

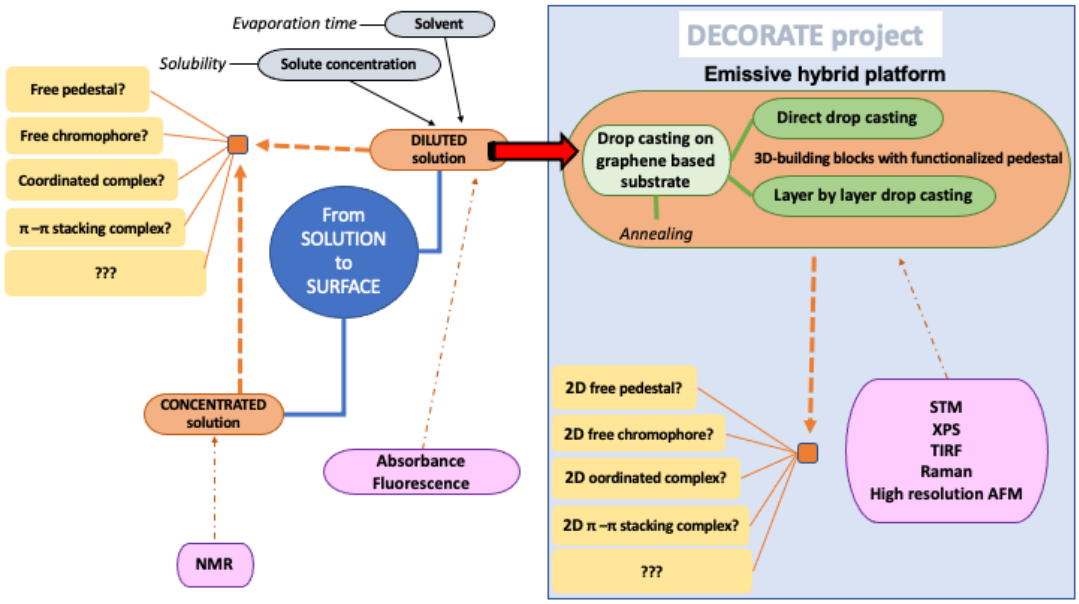
This project proposes, through non-covalent surface functionalization, an easy-to-implement strategy to rationally decorate graphene-based materials in a robust and tunable way with new 3D molecular building blocks composed of a pedestal, a linker and a chromophore in order to obtain light-responsive system for new efficient optoelectronic nanodevices. This project takes advantage of the versatility of phthalocyanine and porphyrin hybrids as pedestals.

Description scientifique / Scientific description (5 pages max.)

Objectifs et description du projet/Objectives and description of the project

This project is part of the general issue which consists in deeply understanding how to transfer the properties of molecules in solution onto surface[1,2]. In order to obtain a fully functional surface from molecular building blocks physisorbed on a 2D substrate, many parameters have to be taken into account like molecule-molecule interactions, molecule-surface interactions, solubility, solute concentration, deposition process, annealing[3]…(see Synopsis).

Through the experience and expertise of **Partner 1**[4-6] and **Partner 3**[7-9], the requested jointly supervised PhD student will explore in a systematic way the influence of various parameters on the physical properties of supramolecular networks on graphene surface of 3D molecules from solution evaporation deposition (drop casting) in order to obtain emissive platforms as it is described in the Synopsis above.



Synopsis : Integration of the DECORATE project in the problem of understanding how the properties of molecules in solution can be transferred to a surface. The question is: "If you know what you have in your solution, do you know what you have on your surface after drop casting?"

Thus, the PhD student will study and optimize the relevant parameters favoring the fabrication of efficient emissive platforms based on 2D supramolecular networks. This requires to achieve the main following tasks : (i) Elaboration of emissive platforms, (ii) Structural characterization of supramolecular networks, (iii) Surface chemistry analysis, and (iv) Detection of optical activity.

The originality of DECORATE ("From solution to surface: 2D-organization of fluorescent functionality on graphene based materials") is based both on the new synthetized molecules carried out by the **Partner 2** and the easy-to-implement strategy for rational decoration of graphene based materials (graphene as a surface is particularly attractive for supramolecular functionalization) with molecular building blocks containing a chromophore[10-12].

Molecular building blocks investigated in this project are 3D molecules (Figure 1a) made up of:

- Functionalized pedestal (substituted phthalocyanines or substituted porphyrins)
- Linker (pyridyl groups)

- Chromophore (where one can tune the distance and the angle with respect to the surface).

So, the design, synthesis and characterization of new phthalocyanines (Pc), porphyrins (P) and perylenediimide (PDI) derivatives as chromophores have been successfully achieved[13].

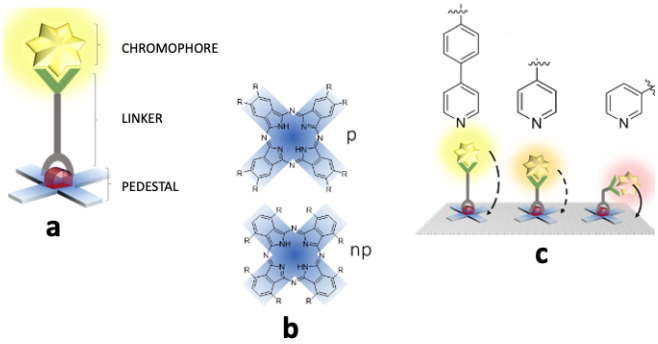


Figure 1: Overview of the DECORATE strategy. ***a*** *3D molecular building block.* ***b*** *Alkyl functionalized Pc molecule at peripheral positions (p) and non peripheral positions (np).* ***c*** *The choice of the linker tunes the distance and the angle between the chromophore and the pedestal*

Recently, **Partner 2** prepared different PDIs where two or four bay-positions have been functionalized with a mono or di-tertbutyl phenol (Figure 2d). This functionalization has been described in the literature and is proven to increase the solubility in polar solvent (toluene or chloroform) by decreasing the aggregation[14,15]. Then, these different functionalized PDIs can tune the distance and the orientation between fluorescent functionality and pedestal (Figure 1c).

The pedestals considered in this study are substituted phthalocyanines and substituted porphyrin functionalized by alkyl chains (Figure 2a-c) which are able to self-organize in a compact way on graphene surface[13] (Figure 2e and 2f). This original approach for functionalization of graphene based materials, such as HOPG (highly oriented pyrolytic graphite) or graphene on copper single crystal, is motivated by the desire to achieve compact, long range, tunable and robust supramolecular networks which is induced both by the physisorption of the aromatic cycles of the pedestals, favored by the planarity of the latter[16], and by a surface epitaxy of the alkyl chains[17,18]. That's why all the Pc and P derivatives will contain zinc as the central metal cation, thus giving them a high planarity (compared to the bigger sized Pb cation). Then, 3D complexes are expected to be obtained via the metal-ligand coordination between the zinc cation within the macrocycle's cavity and the pyridyl functionalities from the PDI derivatives (Figure 1). A covalent approach will also be considered with titanyl Pc molecules (Figure 2). Note that a systematic study of the influence of the annealing of the deposited layers on the stability and robustness of these layers will be carried out. The new phthalocyanines synthesized possess eight linear alkyl chains at the peripheral positions. Chain lengths of six and twelve carbons were chosen to tune the distance between pedestals on the surface. Note that the self-assembled network structure could be tuned by putting linear alky chains at non-peripheral positions (Figure 1b) or by using naphthalocyanine (C6ZnNc) (Figure 2a) and alkyl-porphyrin and alkyl-tetrabenzoporphyrin (Figure 2c) to observe the effect of the size of the conjugated core.

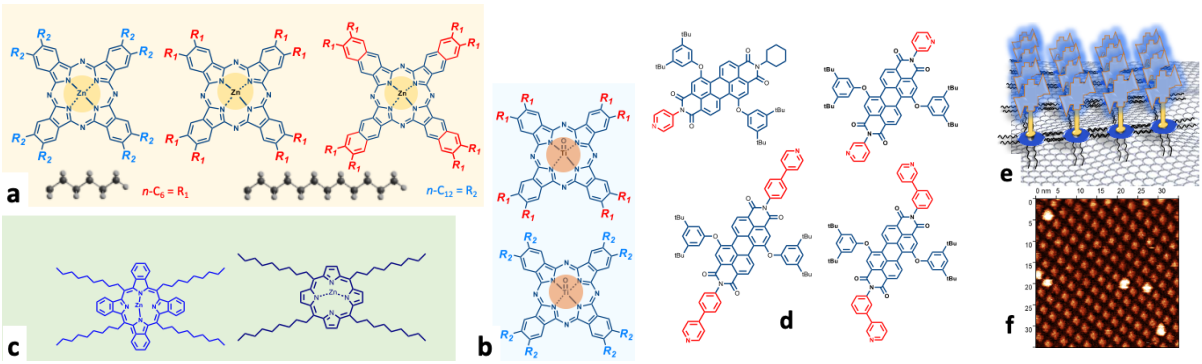


Figure 2: All the molecules involved in DECORATE project. ***a-c*** *Pedestals.* ***d*** *Fluorescent units.* ***e*** *Schematic of compact self-assembled network.* ***f*** *40 x 40 nm STM image of C_{12}ZnPc network + PDI molecules*

Finally, the study and the optimization of the parameters favoring the fabrication of efficient emissive platforms based on 2D supramolecular networks[19] require to characterize the main properties of these 2D networks, *i.e.*, the structural parameters, the surface chemistry and the optical activity. Thus, the other originality of the DECORATE project consists in cross-checking the observations and information gathered by the following experimental techniques:

- Scanning tunneling microscopy, *STM* (*MONARIS, SU*)
  - Observation of supramolecular networks

- High resolution atomic force microscopy, *AFM* (*University of Groningen*)
  - Observation of supramolecular networks
  - No strong potential invasive electrical fields as STM investigations

- Raman spectroscopy (*MONARIS, SU*)
  - Qualitative chemical information

- X-ray photoemission spectroscopy, *XPS* (*University of Groningen / synchrotron facilities: ELETTRA, SOLEIL,…*)
  - Qualitative and quantitative surface chemical information
  - Orientation of the chromophore with respect to the surface

- Total internal reflection fluorescence microscopy, *TIRFM* (*MONARIS, SU*)
  - Observation of fluorescence at nanometer scale
  - Orientation of the chromophore with respect to the surface

Faisabilité. Evaluation et gestion des risques / Feasibility. Risk assessment and management (1/2 page environ*Erreur ! Signet non défini.****)***

The high feasibility rate and the low proportion of risk of the DECORATE project is above all due to the existing strong interactions between **Partner 1** and **Partner 2**, the long-term collaboration between **Partner 1** and **Partner 3** and also the experience and hindsight on the molecular systems involved in DECORATE.

Indeed, the collaborations of **Partner** 1 on the topic "surface functionalization: elaboration and characterization of nanostructured surfaces" with **Partner 2** and **Partner 3** have been settled up for several years, even decades, of which several articles have been the result or are in preparation.

Then, **Partner 1** and **Partner 2** together supervised several Master students (Lydia Hamitouche (2017), Shiva Moradmand (2018)), PhD students (Quentin Fernez (2018), Shiva Moradmand (2019)) and a postdoc (Michele Mattera (2017)) on different projects involving zinc Pc and P molecules, peripheral and non-peripheral alkyl-functionalized Pc Zn and Pb substituted, fluorescent dyes, and nanoporous molecular host-guest template[4] to decorate graphene based materials with 3D molecular building blocks[20].

On the other hand, thanks to **Partner 2**, the molecules envisaged (pedestals and dyes) in the DECORATE project are already available. In addition, **Partner 2** will bring all its experience in the use and supply of molecules while continuing to synthesize new interesting molecules.

Last but not least, since 2019, **Partner 1** is the PhD supervisor of Shiva Moradmand. This doctoral project, entitled "3D-molecular building blocks for functional 2D-supramolecular self-assemblies", is funded by ED 388 and in 2020, **Partner 1** has set up a jointly supervised doctoral thesis with **Partner 3** between Sorbonne Université (SU) and University of Groningen (RUG), The Netherlands. Instead of alkyl functionalized Pc and P derivatives, Shiva Moradmand is using a host-guest template, *i.e.* an organic nanoporous monolayer, to decorate a graphene surface with ZnPc and ZnP molecules as pedestals. In her systematic study, she got plenty of interesting results in STM, Raman spectroscopy and XPS (several papers are in preparation).

Situation du projet sur le plan national et international/Position of the project within national and international context (1/2 page environ)

In order to obtain light-responsive system for new efficient optoelectronic nanodevices[19], DECORATE deals with an easy-to-implement strategy to rationally decorate graphene-based materials in a robust and tunable way through non-covalent functionalization of new 3D complex molecular building blocks composed of a pedestal, a linker and a chromophore to avoid the electronic coupling between the metal substrate and directly adsorbed optically active molecules. Note that the use of alkyl Pc and P functionalized derivatives as a molecular pedestal for surface functionalisation has not yet been reported.

Selective non-covalent interactions have been widely exploited in solution-based chemistry to direct the assembly of molecules into nanometer-sized functional structures and surface-confined molecular self-assembly of organic molecules is a popular approach to create patterned surfaces[1]. But, controlling the organization of building blocks into self-assembled molecular networks at the liquid–solid interface is complex. Solute–solvent and solvent–substrate interactions have to be taken into the account in addition to the interactions between solute–solute and solute–substrate[3]. Furthermore, external experimental conditions such as for example, temperature, pH, electric field and concentration are important parameters defining the outcome of the self- assembly process[3]. Recently, the concepts of supramolecular organization have also been applied to 2D assemblies on surfaces[21]. That's why it is important to get a deep understanding of all the parameters involved when one wants to transfer the properties of molecules in solution onto surface.

DECORATE aims to develop a new and versatile molecular design strategy for the functionalisation of graphene-based materials. The application of functionalized graphene in optoelectronic devices is still at its early stages and a lot of work is still to be done on fundamental exploration[19]. The main challenge with graphene is to control the growth and organization of molecular films to enhance the performance of optoelectronic devices. Because graphene is a good substrate to grow supramolecular self-assemblies, many nanodevices based on organization organic molecules can now be developed for the broad application of organic semi-conducting materials in the OLED, OFET and OPV fields[19].

Finally, as proof of the interest that the subject of DECORATE can arouse in the scientific community, we can mention that within the framework of Shiva Moradmand's co-supervised thesis (**Partner 1** and **Partner 3**), 4 proposals for obtaining beamtime at the ELETTRA Synchrotron in Trieste (Italy) have been accepted in 2021 and 2022, and this, on 3 different beamlines:

1. July 2021 (21^{st} to 26^{th}): Material Science Beamline (XPS and NEXAFS)
2. October 29^{th} 2021 to November 3^{rd} 2021: VUV Beamline (XPS)
3. March 2022 (8^{th} to 12^{th}): Material Science Beamline (XPS and NEXAFS)
4. May 2022 (8^{th} to 12^{th}): ALOISA Beamline (XPS and absorption spectroscopy)

*Positionnement du projet par rapport aux objectifs de l'iSiM/Position of the project in regard to the iSiM objectives (1/2 page environ*Erreur ! Signet non défini.*)*

The DECORATE project is completely in line with "les Sciences et Ingénierie Moléculaires" since it relies on the use of multi-component 3D molecules to create 2D emissive platforms. As it was partly mentioned above, the federative and transversal character (Polymer Chemistry vs. Surface Science, *i.e.* Solution vs. Surface) as well as the association of skills (fabrication of self-assembled monolayer networks + structural properties + surface chemistry + optical characterization) are clearly established. We can still go further, by specifying that the DECORATE project will make it possible to develop research of excellence between teams of the "Alliance Sorbonne Université" and outside, at three different levels: (i) within MONARIS, (ii) between NARCOS team (MONARIS) and ECP team (IPCM) and (iii) at the international level with the presence of Surface and Thin Films group from the University of Groningen (The Netherlands).

Faire apparaitre la complémentarité des compétences/ Highlight partners complementarity

The skills of each partner will contribute effectively and harmoniously to the achievement by the PhD student of the main tasks of the project DECORATE (see the Research program section), *i.e.* (i) Elaboration of emitting hybrid platforms, (ii) Structural characterization of supramolecular networks, (iii) Surface chemistry analysis, and (iv) Detection of optical activity.

DECORATE will promote a synergistic partnership between the topics of Synthetic Chemistry and Surface Science. As it has already mentioned, one of the main originality of this project consists in cross-checking the observations and information gathered by several experimental techniques, going from Raman spectroscopy to TIRF microscopy or from XPS setup located at laboratory to XPS facilities at synchrotron. This highlight partners complementarity is made possible by the existence of strong interactions between **Partner 1** and **Partner 2**, the long-term collaboration between **Partner 1** and **Partner 3** and also the experience and hindsight on the molecular systems involved in DECORATE.

Références / Bibliography

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2 Mali, K. S., Pearce, N., De Feyter, S. & Champness, N. R. Frontiers of supramolecular chemistry at solid surfaces. *Chemical Society Reviews* **46**, 2520-2542, doi:10.1039/c7cs00113d (2017).

3 Mali, K. S., Adisoejoso, J., Ghijsens, E., De Cat, I. & De Feyter, S. Exploring the Complexity of Supramolecular Interactions for Patterning at the Liquid-Solid Interface. *Accounts of Chemical Research* **45**, 1309-1320, doi:10.1021/ar200342u (2012).

4 Kim, B. *et al.* 2D host-guest supramolecular chemistry for an on-monolayer graphene emitting platform. *Materials Horizons* **7**, 2741-2748, doi:10.1039/d0mh00950d (2020).

5 Bleger, D. *et al.* Periodic Positioning of Multilayered 2.2 Paracyclophane-Based Nanopillars. *Angewandte Chemie-International Edition* **47**, 8412-8415, doi:10.1002/anie.200801335 (2008).

6 van den Brom, C. R. *et al.* Selective immobilization of nanoparticles on surfaces by molecular recognition using simple multiple H-bonding functionalities. *Advanced Functional Materials* **17**, 2045-2052, doi:10.1002/adfm.200600497 (2007).

7 Gottardi, S. *et al.* Comparing Graphene Growth on Cu(111) versus Oxidized Cu(111). *Nano Letters* **15**, 917-922, doi:10.1021/nl5036463 (2015).

8 Zhang, X. Y. *et al.* One-Pot Functionalization of Graphene with Porphyrin through Cycloaddition Reactions. *Chemistry-a European Journal* **17**, 8957-8964, doi:10.1002/chem.201100980 (2011).

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10 Kim, B. *et al.* 2D host-guest supramolecular chemistry for an on-monolayer graphene emitting platform. *Materials Horizons* **7**, 2741-2748, doi:10.1039/d0mh00950d (2020).

11 Brisse, R. *et al.* Probing the in-air growth of large area of 3D functional structures into a 2D supramolecular nanoporous network. *Chemical Communications* **54**, 10068-10071, doi:10.1039/c8cc06125d (2018).

12 Sosa-Vargas, L., Kim, E. & Attias, A. J. Beyond "decorative" 2D supramolecular self-assembly: strategies towards functional surfaces for nanotechnology. *Materials Horizons* **4**, 570-583, doi:10.1039/c7mh00127d (2017).

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Programme de travail /

Programme de recherche / Research program (1 page max.)

Highly motivated candidates (expecting a master degree or equivalent with excellent academic records) with a background in Physical Chemistry and Material Science are strongly encouraged to apply. Knowledge of the candidate in scanning probe microscopies (STM and/or AFM), X-ray photoemission spectroscopy (XPS), and/or Raman spectroscopy will also be appreciated. Previous laboratory experience in synchrotron facilities, surface functionalization, nanomaterials, supramolecular architectures or any other field that could benefit the project would be valuable but is not mandatory.

Through a jointly supervised doctoral thesis (**Partner 1** and **Partner 3)** between Sorbonne Université (SU) and University of Groningen (RUG), the PhD student will study and optimize the relevant parameters favoring the fabrication of efficient emissive platforms based on 2D supramolecular networks. This requires to achieve the main following tasks : (i) Elaboration of emitting hybrid platforms, (ii) Structural characterization of supramolecular networks, (iii) Surface chemistry analysis, and (iv) Detection of optical activity. Here is the provisional timetable for the completion of these tasks:

Functional 2D supramolecular networks on graphene 3D building blocks with functionalized pedestal and fluorescent unit		1st year ***SU***		2nd year ***RUG***		3rd year ***SU***	
Fabrication	Direct vs. Layer by layer drop casting	■	■	■	■	■	
	Annealing of the deposited layer	■	■	■	■	■	
	Different pedestals / fluorescent units	■	■	■	■	■	
Structural parameters	STM at air-solid interface	■	■			■	
	High resolution AFM			■	■		
Surface chemistry	Raman spectroscopy	■	■				
	XPS (laboratory)			■	■		
	XPS (Synchrotron)		■	■	■		
Optical activity	TIRF microscopy		■			■	
Work outputs	Bibliography / State of the art…	■	■	■	■	■	■
	Regular reports	■	■	■	■	■	
	Posters / Seminars / Articles		■	■	■	■	■
	Writing / Defense						■

The 10,000 euros attached to the ISIM doctoral grant will facilitate the travels of the future PhD student.