Proposition de sujet de thèse en cotuelle financée
Jointly supervised PhD project
Sorbonne Université / University of Groningen

Titre : *Étude et optimisation des paramètres favorisant la fabrication de plateformes émissives performantes basées sur des réseaux supramoléculaires 2D physisorbés sur du graphène*

Title *: From solution to surface: 2D-organization of fluorescent functionality on graphene based materials*

Mots clés : *Fonctionnalisation de surface, Auto-assemblage moléculaire, Graphène, Phtalocyanine, Porphyrine, Fluorescence, STM, XPS, AFM, TIRFM*

Keywords : *Surface functionalization, Supramolecular self-assembly, Graphene, Phthalocyanine, Porphyrin, Fluorescence, STM, XPS, AFM, TIRFM*

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Résumé

Grâce à la fonctionnalisation non covalente des surfaces, ce projet propose une stratégie facile à mettre en œuvre pour décorer, de façon rationnelle et de manière robuste et modulable, le graphène avec des briques moléculaires 3D originales qui sont composées d'un socle et d'un fluorophore, liés par une molécule versatile. Cela afin d'obtenir des systèmes sensibles à la lumière pour la fabrication de nouveaux nanodispositifs optoélectroniques améliorés. Ce projet tire parti de la polyvalence des composées dérivés de phtalocyanine et de porphyrine utilisées ici comme socles. Ainsi, l'étude et l'optimisation des paramètres favorisant la fabrication de plateformes émissives performantes à base de réseaux supramoléculaires 2D sur du graphène nécessitent de caractériser les principales propriétés de ces réseaux 2D, à savoir les paramètres structuraux, la chimie de surface et l'activité optique. Ce projet consistera alors à recouper les observations et informations recueillies par plusieurs techniques expérimentales comme la microscopie à effet tunnel (STM), la microscopie à force atomique à haute résolution (AFM), la spectroscopie Raman, la spectroscopie de photoémission par rayons X (XPS) et la microscopie de fluorescence par réflexion totale interne (TIRFM).

Summary

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. The study and the optimization of the parameters favoring the fabrication of efficient emissive platforms based on 2D supramolecular networks require to characterize the main properties of these 2D networks, i.e., the structural parameters, the surface chemistry and the optical activity. Thus, this project consists in cross-checking the observations and information gathered by several experimental techniques as scanning tunneling microscopy (STM), high resolution atomic force microscopy (AFM), Raman spectroscopy, X-ray photoemission spectroscopy (XPS), and total internal reflection fluorescence microscopy (TIRFM).

Project description and objectives

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]…Through the experience and expertise of I.A.[4-6] and P.R.[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. Thus, the applicant 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. Molecular building blocks investigated in this project are 3D molecules[10] (Figure 1a) made up of functionalized pedestal (substituted phthalocyanines or substituted porphyrins) (Figure 1b) and a chromophore ad then one can tune the distance and the angle with respect to the surface through a pyridyl group (Figure 1c).

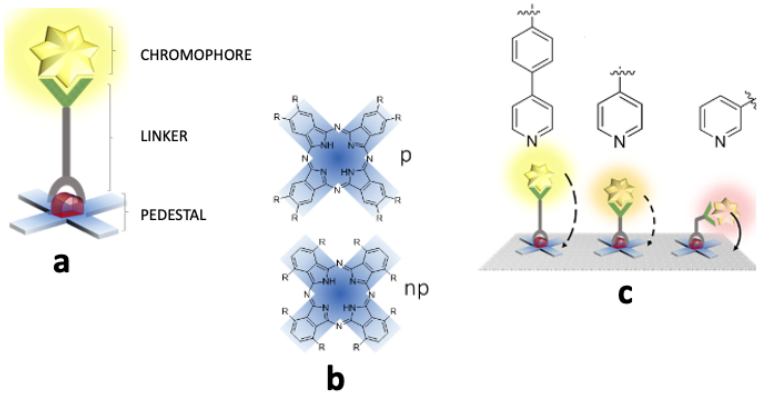

Figure 1: Overview of the project strategy. ***a*** *3D molecular building block.* ***b*** *Alkyl functionalized Pc molecule at peripheral positions (p) and non peripheral positions (np).* ***c*** *The choice of the linker tunes the distance and the angle between the chromophore and the pedestal*

The originality of this project is based both on the new synthetized molecules carried out by L.S.V. 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]. The other originality of the 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

The applicant will stay 2 years in Paris and 1 year in Groningen.

References

1 Theobald, J. A. *et al.*, *Nature* **424**, 1029-1031 (2003).
2 Mali, K. S. *et al.*, *Chemical Society Reviews* **46**, 2520-2542 (2017).
3 Mali, K. S. *et al.*, *Accounts of Chemical Research* **45**, 1309-1320 (2012).
4 Kim, B. *et al.*, *Materials Horizons* **7**, 2741-2748, doi:10.1039/d0mh00950d (2020).
5 Bleger, D. *et al.*, *Angewandte Chemie-International Edition* **47**, 8412-8415 (2008).
6 van den Brom, C. R. *et al.*, *Advanced Functional Materials* **17**, 2045-2052 (2007).
7 Gottardi, S. *et al.*, *Nano Letters* **15**, 917-922 (2015).
8 Zhang, X. Y. *et al.*, *Chemistry-a European Journal* **17**, 8957-8964 (2011).
9 Quintana, M. *et al.*, *Acs Nano* **4**, 3527-3533, doi:10.1021/nn100883p (2010).
10 Sosa-Vargas, L. *et al.*, *Materials Horizons* **4**, 570-583 (2017).

Candidate profile and applications

Highly motivated candidates (expecting a Master 2 degree or equivalent with excellent academic records in Physics, Engineering, Material Science or related areas) with a background in Physical Chemistry and Material Science are strongly encouraged to apply. Knowledge (and strong interest) of the candidate in scanning probe microscopies (STM and/or AFM), X-ray photoemission spectroscopy (XPS), and/or Raman spectroscopy will also be expected. Previous 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.

Candidates must have a good knowledge of English as well as good communication skills. Applications including a cover letter, a curriculum vitae, academic records, should be sent to imad.arfaoui@sorbonne-universite.fr. Recommendations (with contact details) will also be appreciated.