



# Electrografting and Langmuir–Blodgett: Covalently Bound Nanometer-Thick Ordered Films on Graphite

Jérôme Médard, Xiaonan Sun, Jean Pinson, Da Li, Claire Mangeney,  
Jean-Philippe Michel

## ► To cite this version:

Jérôme Médard, Xiaonan Sun, Jean Pinson, Da Li, Claire Mangeney, et al.. Electrografting and Langmuir–Blodgett: Covalently Bound Nanometer-Thick Ordered Films on Graphite. *Langmuir*, In press, 37 (43), pp.12539-12547. 10.1021/acs.langmuir.1c01723 . hal-03402711

**HAL Id: hal-03402711**

**<https://hal.science/hal-03402711>**

Submitted on 25 Oct 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - ShareAlike 4.0 International License

# Electrografting and Langmuir-Blodgett: Covalently Bound Nanometer Thick Ordered Films on Graphite

Jérôme Médard<sup>a</sup>, Xiaonan Sun<sup>a</sup>, Jean Pinson<sup>a,\*</sup>, Da Li<sup>c</sup>, Claire Mangeney<sup>c</sup>, Jean-Philippe Michel<sup>b,\*</sup>

<sup>a</sup> Université de Paris, ITODYS, CNRS, UMR 7086, 15 rue J-A de Baïf, F-75013 Paris, France.

<sup>b</sup> Université Paris Saclay, Institut Galien Paris Saclay, CNRS, UMR 8612, 5 rue Jean-Baptiste Clément, F-92296 Châtenay-Malabry, France.

<sup>c</sup> Université de Paris, UMR 8601, CNRS, 45 rue des Saints Pères, 75006 Paris, France.

\*Corresponding authors:

[jean.pinson@univ-paris-diderot.fr](mailto:jean.pinson@univ-paris-diderot.fr)

[jean-philippe.michel@universite-paris-saclay.fr](mailto:jean-philippe.michel@universite-paris-saclay.fr)

## Abstract

We present two different molecular organizations obtained from octadecylamine (ODA) molecules on Highly Oriented Pyrolytic Graphite (HOPG) surface: i) self-organized physisorbed ODA molecules lying flat on the surface and ii) strongly electrografted compact crystalline monolayer of ODA molecules standing up on the surface. This new structure is obtained by combining the Langmuir-Blodgett transfer of an ODA Langmuir film onto HOPG with oxidative electrografting. The presence of organic film on HOPG is characterized by ATR-IR (Attenuated Total Reflectance- Infrared Spectroscopy) and Raman spectroscopies, while Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) allow the observation of the two molecular organizations, with adsorbed molecules lying flat on HOPG or strongly grafted in an upright position on the HOPG surface. Interestingly, the second molecular organization preserves a hexagonal symmetry and its lattice parameters are intermediate between those of ODA Langmuir films and that of HOPG underlying surface. The functionalization of surfaces with organic films is a major issue in the design of sensors with biomedical applications, or organic electronics and energy storage devices and these structures may find applications in these fields.

## Introduction

In view of vast panorama of organic molecules able to be immobilized on surfaces, several surface functionalization strategies have been developed over time. A first group of methods relies on physical adsorption, such as Langmuir-Blodgett layers on surfaces. Langmuir films are bidimensional systems in which amphiphile molecules are compressed on a water surface to provide crystalline monolayer structures, such as ODA. These films can be transferred (Langmuir Blodgett films<sup>1</sup>) onto a solid surface: Si,<sup>2,3</sup> mica,<sup>4</sup> inorganic substrates,<sup>5</sup> glass or quartz substrates,<sup>6</sup> and HOPG (Highly Oriented Pyrolytic graphite),<sup>7</sup> on which they can form adsorbed crystalline structures. The crystal structure of the film can be demonstrated by GIXD (Grazing Incidence X-ray Diffraction)<sup>8,9,10,11</sup>, surface morphology and molecular organization by Atomic Force Microscopy (AFM)<sup>12,13</sup> or Scanning Tunneling Microscopy (STM)<sup>14</sup>. Other approaches involving physical adsorption of molecules generally lead to disordered structures, but perfectly organized self-assembled molecules (alkanes, aromatic compounds) are obtained on crystalline lattice defined surfaces, which can be observed by AFM and STM. The surfaces that are most often used for this purpose are HOPG<sup>15,16,17,18,19</sup> and oriented Au (111)<sup>20,21</sup>.

A second group of approaches yield grafted (chemically adsorbed) molecules for which a bond of variable energy is obtained between the surface and the organic molecules; among them thiols on gold provide organized monolayers imaged by local probe microscopies such as STM.<sup>22,23</sup> The possible organization is related to the mobility of thiols on a gold surface.

On surface oxides,<sup>24</sup> such as TiO<sub>2</sub>, ZrO<sub>2</sub>,<sup>25</sup> glass or quartz,<sup>26,27</sup> silanes provide strong Si-O bonds but do not generally provide organized surfaces as the strong covalent bond does not permit molecules to move and rearrange on the surface. Phosphonic and carboxylic acids, as well as catechols also bind to oxide surfaces.<sup>24</sup>

Electroreduction of diazonium salts,<sup>28,29</sup> alkyl halides,<sup>30</sup> and azosulfones<sup>31</sup> or oxidation of amines,<sup>32</sup> generally lead to grafted disordered oligomers (so-called multilayers) strongly bonded on different surfaces. These modified surfaces were mainly characterized by X-ray photoelectron spectroscopy (XPS), IR and Raman spectroscopies. All these grafting reactions involve a radical as a key intermediate; this radical reacts with the surface but also with the first grafted layer leading to surface bonded oligomers. The possibility to control the thickness of the films permit different interesting applications, for example thick layers are useful in carbon fiber-epoxy composites where they increase the interfacial shear strength;<sup>33</sup> while monolayers are useful in biosensors,<sup>34</sup> and organic microelectronics.<sup>35</sup>

Monolayers can be obtained using electrochemistry by controlling operational parameters (reaction time, applied potential, concentration), or by tuning the reactivity of the radical in

different ways: i) using steric effects (starting from sterically hindered diazonium salts with two 3,5 bis-*t*-butyl groups or a 4-((triisopropylsilyl)<sup>36</sup> group), ii) using viscous ionic liquids that reduce the diffusion rates to the surface<sup>37</sup>, iii) using redox mediators that limit the concentration of radicals in the vicinity of the electrode<sup>38</sup>. STM<sup>39</sup> and AFM<sup>38</sup> images confirm the expected thickness but indicate the absence of organization. However the above methods only limit the growth of the films. A very limited number of papers report the formation of organized monolayers from bulk solution: a film of an organized Ru complex has been built on HOPG by electrochemistry and imaged by STM;<sup>40</sup> on graphene, under visible light a film of phenazine with a short-range order has been characterized in the same way.<sup>41</sup>

It is therefore interesting to find out a method that permits to obtain monolayers by construction and not by reducing the reactivity of the radical or controlling their concentration. In addition, conferring both a strong bonding and a crystalline structure to an organic film is an interesting challenge to create stable and organized monolayers covering surfaces with biotechnological or biomedical interest. This challenge can be taken on by combining different methods of molecular immobilization on surfaces. For example, an octadecylamine Langmuir film transferred to a gold surface by the Langmuir-Blodgett technique under oxidative potential permits to obtain a strongly bonded organic film with a crystalline order. This order is limited due to the structural nature of gold surface where crystalline domains are very small (20-50 nm).<sup>42</sup> In order to increase the order, this work investigates HOPG as an ordered surface for the transfer of the LB film, to take advantage of the large monocrystalline domains that can be observed in this material. We seek whether the monocrystalline structure of HOPG domains could impact the ordering of octadecylamine deposited onto it using the same process combining Langmuir-Blodgett transfer and electrografting under oxidative potential.

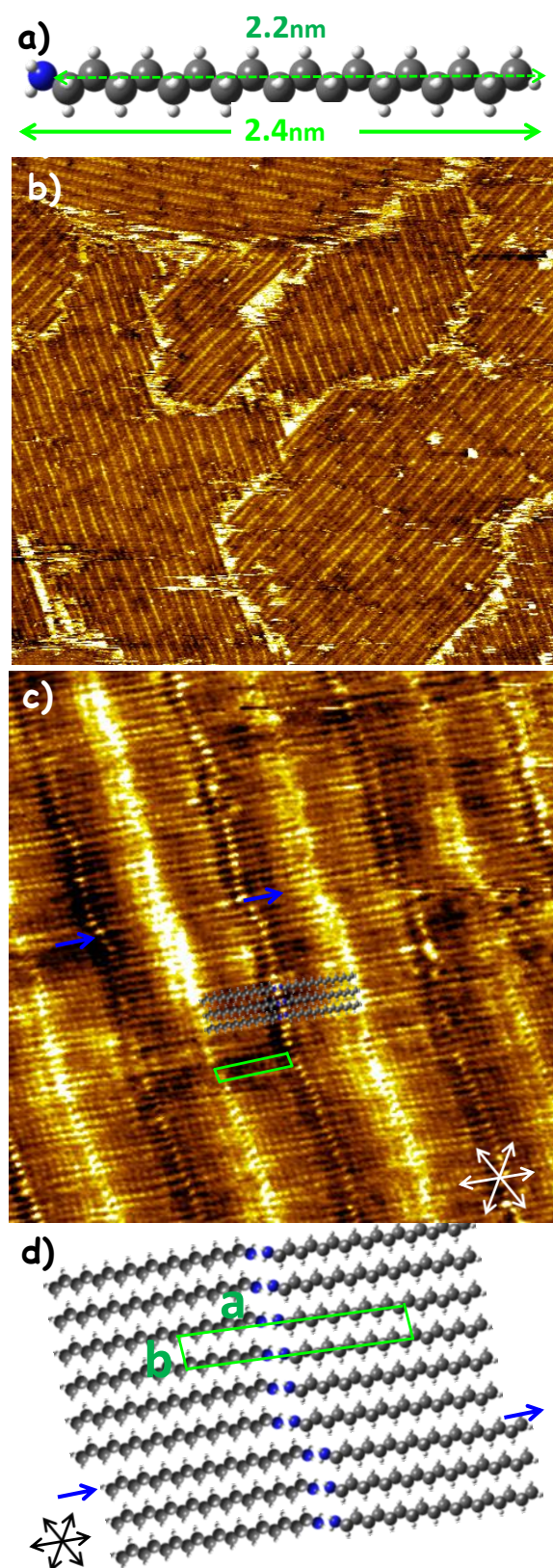
This work presents two different molecular organizations of octadecylamine (ODA) molecules on HOPG surface: i) the self-organized ODA film with molecules physisorbed flat on the surface and ii) the same molecule standing up and chemically grafted to the surface of HOPG. This last structure is obtained by combining the Langmuir-Blodgett transfer of an ODA Langmuir film onto HOPG and simultaneous electrografting as previously described (LB-eG process).<sup>32,42</sup> The presence and identification of the film is characterized by IR, XPS and Raman spectroscopies while SFM and AFM allow the observation of the two organized structures either adsorbed and lying flat, or strongly grafted in a crystalline monolayer.

## Results

### ***ODA adsorbed on HOPG by drop deposition***

ODA was solubilized in 1-heptanoic acid and a drop deposited on HOPG surface. The resulting HOPG surface was then imaged by STM at the solid/liquid interface. ODA molecule has a full stretched length around 2.4 nm (Figure 1a). Large scale STM image presented in Figure 1b reveals a highly ordered lamellar supramolecular structure, in which different 100 nm size domains co-exist on the surface, and demonstrates that ODA molecules can self-assemble by drop deposition from organic solution at room temperature at the solvent/HOPG interface. Angles of 60 or 120° are measured between the different monocrystalline domains. Inside domains, ODA molecules self-assemble as two dimensional ribbons in which ODA straight chains are in parallel alternations.

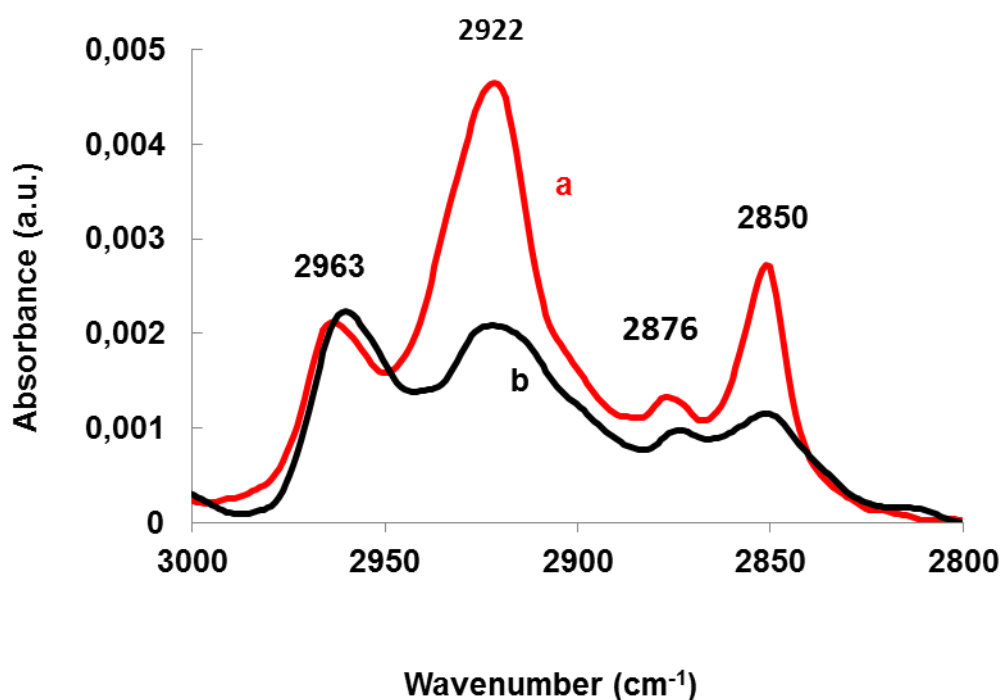
Single ODA molecules are resolved with atomic resolution and molecule models are superimposed in the STM image in Figure 1c. Each ODA molecular chain appears to contain 9 bright spots which correspond to its 18 carbon atoms. This is due to the well-known effect that the two neighboring carbon atoms contribute to only one bright signal with enhanced electron density of state (DOS). The ODA chains are aligned along the HOPG [100] orientation to maximize the molecular/substrate van de Waals interactions as marked by the three symmetry arrows in Figures 1c and 1d. The molecules are stabilized head-to-head through typical N···H-N hydrogen bonds together with the parallel inter-chain and chain/HOPG Van der Waals forces as shown in the plausible models in Figure 1c. Small bending of the lamellar stripe is observed from time to time (as marked by blue arrows in Figures 1c and 1d) arising from a molecular shift along the molecular chains orientation (HOPG [100] crystallographic direction). The unit cell of the lamella structure is marked by green parallelogram shape in Figures 1c and 1d. The lattice parameters are 2.4 (a) and 0.4 (b) nm with an angle of 86°. Each ODA chain is deduced to have a lateral length of around  $2.4 \pm 0.2$  nm which is in good agreement with the theoretical length (calculated by Ampac) of the molecule depicted in Figure 1a. The STM images thus reveal that the physisorbed ODA molecules are lying flat on the HOPG surface.



**Figure 1:** a) A stick-ball molecular model of the ODA molecule. STM images of ODA adsorbed on 1-heptanoic acid/HOPG interface with tunneling parameters  $I_t = 20\text{--}40$  pA,  $U_s = -400\sim -500$  mV, b)  $190\times 183$  nm<sup>2</sup>, c)  $12\times 12$  nm<sup>2</sup>. d) a plausible model is proposed to interpret the observed lamellar structure.

### ***ODA monolayer on HOPG by combining LB technique and electrografting***

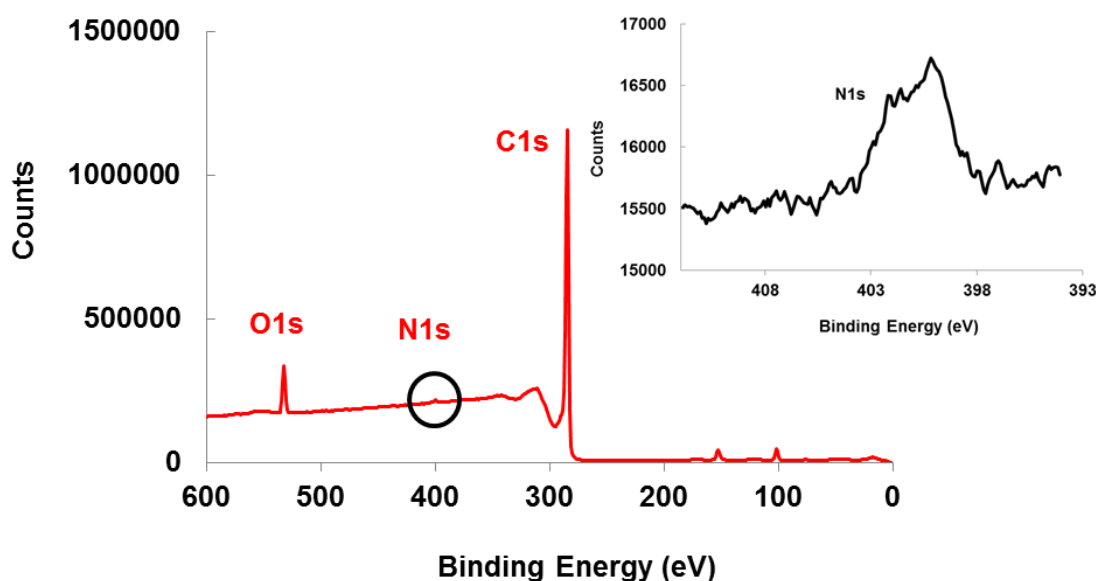
In this experiment, as previously described,<sup>42</sup> the Langmuir trough is used as the electrochemical cell, with the freshly cleaved HOPG surface partly immersed in the trough and used as the working electrode. A saturated calomel electrode (SCE) and a carbon paper counter electrode are also introduced in the water subphase (pH 9). After ODA deposition on the water surface from a spreading organic solution, compression is started after 15 minutes and surface pressure in the ODA film increased up to 40 mN/m. The LB transfer of the ODA LB film onto the HOPG surface is then performed at  $40 \pm 0.2$  mN/m and 0.25 mm/min, simultaneously with chronoamperometry at  $E = +0.85$  V/SCE and stops when the surface is fully removed from the subphase. This sample is denoted as *HOPG-ODA<sub>LB-eG</sub>*.



**Figure 2:** ATR-IR spectrum of *HOPG-ODA<sub>LB-eG</sub>* (a, red curve-absorbance x5) and IRRAS spectrum of *Au-ODA<sub>LB-eG</sub>* (b, black curve).<sup>42</sup>

*ATR-IR spectrum.* The grafted surface obtained by transferring the ODA Langmuir film to the HOPG surface under oxidative potential (*HOPG-ODA<sub>LB-eG</sub>*) was thoroughly rinsed with alcohol and acetone and an ATR-IR spectrum was then recorded and compared to the same ODA monolayer grafted on gold surface, *Au-ODA<sub>LB-eG</sub>*<sup>42</sup> (Figure 2). Both spectra present the same CH antisymmetric (2963, 2922 cm<sup>-1</sup>) and symmetric (2876, 2850 cm<sup>-1</sup>) stretching bands which were previously attributed, on gold, to a partly organized monolayer.<sup>42</sup>

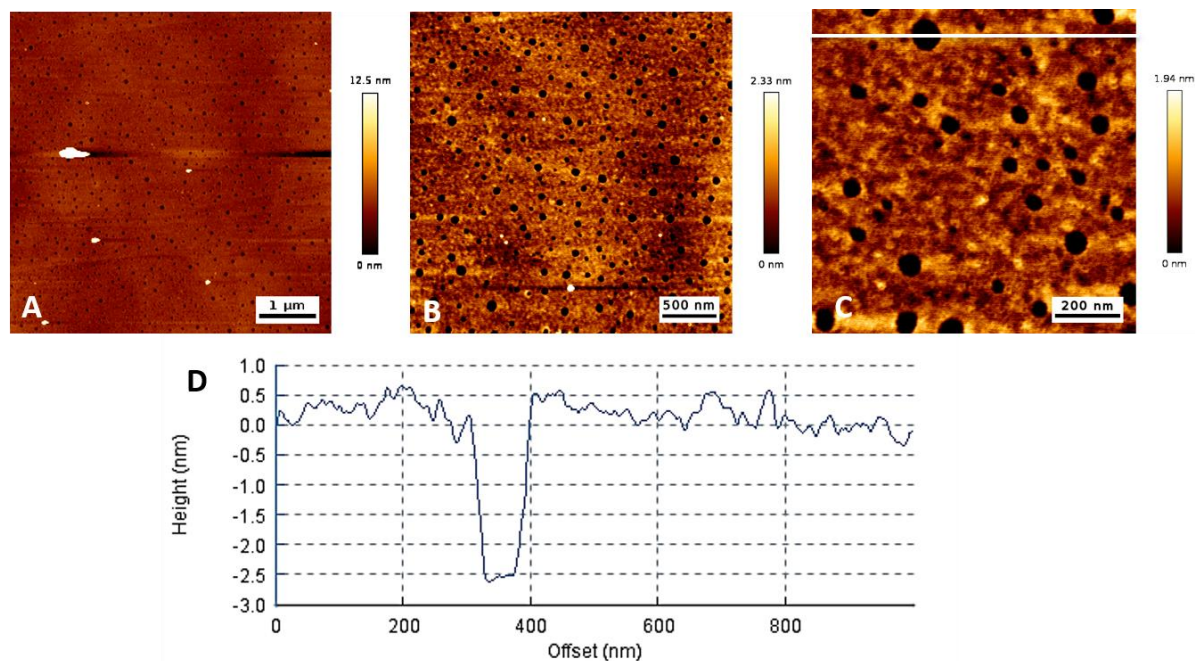
XPS. XPS spectrum of  $\text{HOPG-ODA}_{\text{LB-eG}}$  is presented in Figure 3. The spectrum allows the identification of C1s (93.1%), O1s (6.0%) and N1s (0.9%). C1s strong signal mostly arises from the underlying HOPG carbon atoms surface but also from the C18 carbon chain of ODA. The presence of N1s signal at 400 eV (inset in Figure 4) testifies from the presence of an ODA group on the HOPG surface. O1s signal is attributed to some contamination. Peaks at 100 and 150 eV are Si2p and Si2s signatures, also considered as impurities from HOPG surface.



**Figure 3:** XPS spectrum of  $\text{HOPG-ODA}_{\text{LB-eG}}$ . N1s peak appearing at 400 eV (black circle) is shown as an inset.

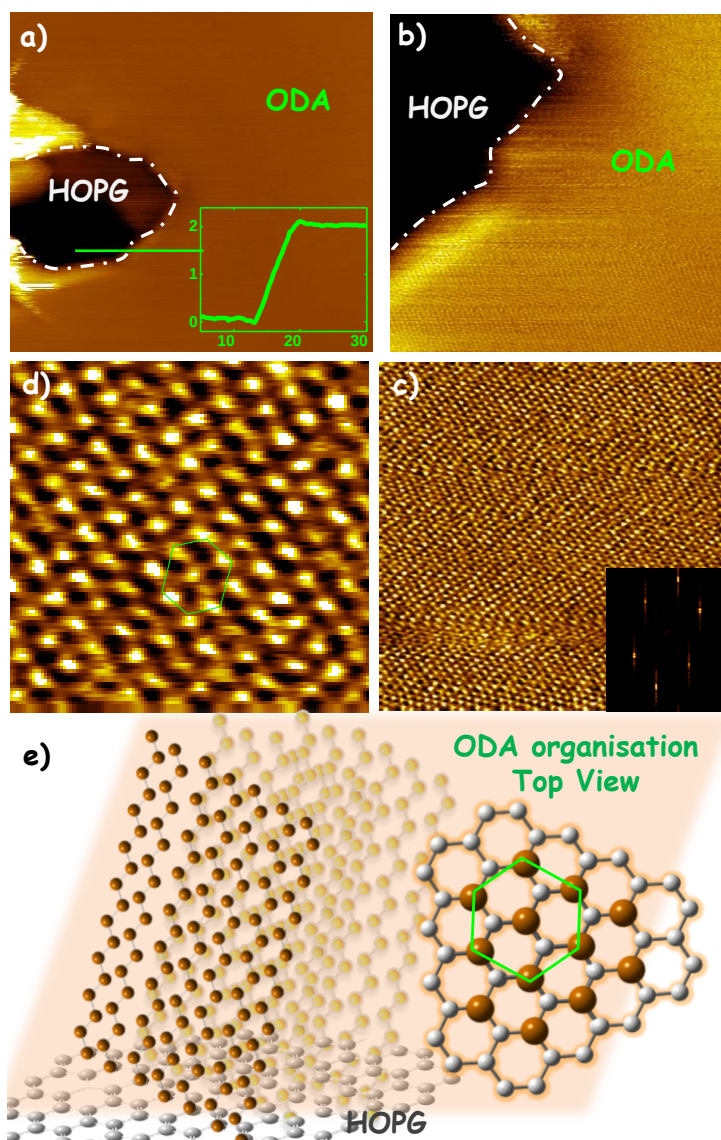
*AFM imaging of  $\text{HOPG-ODA}_{\text{LB-eG}}$ .* HOPG surface was imaged by AFM in air in AC mode after the LB transfer and simultaneous electrografting of ODA monolayer. Figure 4 presents a uniform film covering the whole HOPG surface. Very few small ODA globules adsorbed onto the ODA grafted film could be detected, appearing as white dots in Figure 4A. At smaller scales (Figures 4B and 4C), the ODA film was discontinuous since circular holes are observed homogeneously dispatched on the surface. Most of them have lateral dimensions around 20 nm, but a few holes are larger with diameters up to 60 nm (Figure 4C). Analysis of surface area occupied by these holes in  $1 \mu\text{m}^2$  pictures led to the value of  $6 \pm 2\%$  of their total surface area. Height cross sections performed along holes in the ODA grafted layer (Figure 4D) permitted to obtain the thickness of the film:  $2.5 \pm 0.2 \text{ nm}$  ( $n = 12$ ), a value that corresponds to the length of a fully stretched ODA molecule in the upright position (2.4 nm from a

molecular model). The surface roughness of  $HOPG-ODA_{LB-eG}$  grafted monolayer is 250 pm for defect-free HOPG areas.



**Figure 4:** AFM height images in air of  $HOPG-ODA_{LB-eG}$  at three different scales: (A)  $5 \mu m^2$ , (B)  $2 \mu m^2$  and (C)  $1 \mu m^2$ . The height cross section is taken along the white line drawn in picture C and shows the thickness of  $HOPG-ODA_{LB-eG}$  film.

*STM imaging of  $HOPG-ODA_{LB-eG}$ .* AFM imaging revealed the monomolecular thickness of  $HOPG-ODA_{LB-eG}$  film covering HOPG surface. In order to get insight into any organization of ODA molecules grafted onto HOPG surface at the angstrom scale, STM investigation was then performed in air. Large scale image shows that the circular holes (as observed in the above AFM images in Figure 4) of the grafted layer are also visible under STM, as marked by the white dashed line depicted in Figure 5a. The measured step height between the hole and the layer is about  $2.2 \pm 0.1$  nm, which is close to the ODA molecular length in fully stretched configuration but is very different from a HOPG single step height (around 0.34 nm). Using the circular hole as a signature of the ODA deposition, STM image in Figure 5b shows that the ODA layers seem to be organized in a single domain. No domain boundaries are observed as those shown in the flat self-organization in Figure 1b. Higher resolution STM image (zoomed in on the top layer) exhibits a surprisingly perfect 2D ordering as shown in Figure 5c.

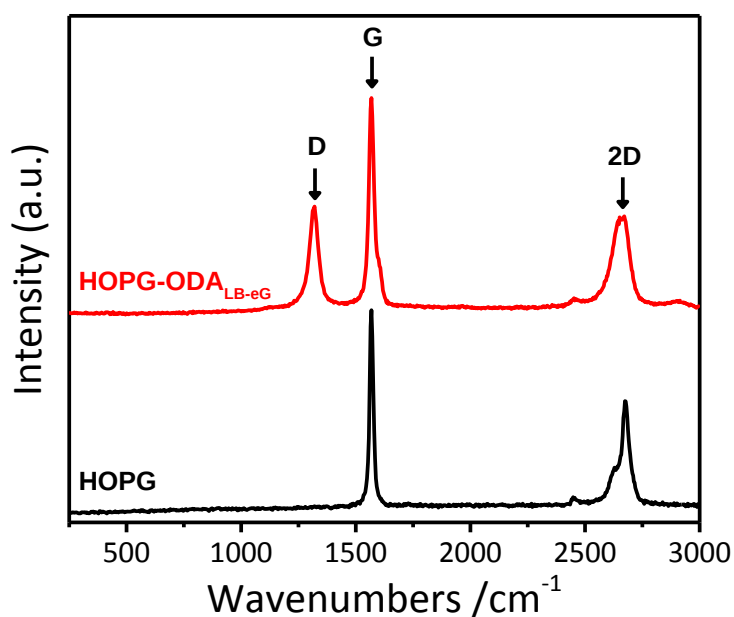


**Figure 5:** STM image of  $HOPG-ODA_{LB-eG}$  with tunneling parameters  $I_t=20-30$  pA,  $U_s= \sim 500$  mV. At large scale: a)  $70 \times 66$  nm<sup>2</sup> b)  $19 \times 19$  nm<sup>2</sup>, high resolution: c)  $9 \times 9$  nm<sup>2</sup>, d)  $2 \times 2$  nm<sup>2</sup>. e) a plausible model is proposed to interpret perpendicularly grafted  $ODA_{LB-eG}$  molecules depicted in orange balls, whereas HOPG carbon atoms are schemed as white balls.

A Fast Fourier Transform (FFT) pattern (inset in Figure 5c) generated from Figure 5c appears as a distorted hexagon with a small twist due to the soft scanning drift from the microscope. The sharp resolution of the FFT pattern depicts a high ordering of the ODA layer. A honeycomb atomic pattern is resolved from a  $2 \times 2$  nm<sup>2</sup> image in Figure 5d, in which the hexagonal lattice is marked in green color with a measured lattice constant of around  $2.3 \pm 0.5$  Å. Note that the tunneling parameters for  $HOPG-ODA_{LB-eG}$  ( $I = 20-50$  pA,  $U = 400-500$  mV)

is quite different than that for bare HOPG surface imaging ( $I = 100\text{-}1000$  pA,  $U = 100\text{-}300$  mV). This difference may be due to a higher conductivity of the bare HOPG surface, which is hampered in  $\text{HOPG-ODA}_{\text{LB-eG}}$  as the insulating ODA monolayer covers the surface.

Plausible models of the ODA organization with respect to the HOPG surface are proposed in Figure 5e. Molecules are grafted perpendicular to the HOPG top layer since the measured height of the ODA layer is exactly the ODA molecular length as previously demonstrated by both AFM and STM characterizations. Top view model indicates that the ODA molecules decorate alternatively three C atoms out of the six from the graphite hexagon unit cell, which gives the ODA honeycomb lattice constant values around  $2.3 \text{ \AA}$ . This cell constant is larger than the HOPG cell constant ( $1.42 \text{ \AA}$ )<sup>43</sup> but is identical to the HOPG bright-to-bright atomic signal distance although the ODA organization is different from that of the HOPG surface.



**Figure 6:** Raman spectra of bare HOPG (black) and  $\text{HOPG-ODA}_{\text{LB-eG}}$  (red). The spectra were recorded using a laser at 638 nm.

*Raman spectroscopy of  $\text{HOPG-ODA}_{\text{LB-eG}}$ .* Raman spectroscopy was used to analyze surface lattice sites and hybridization of HOPG after ODA grafting. Pristine HOPG exhibits two main Raman peaks (Figure 6) at  $1568 \text{ cm}^{-1}$  and  $2675 \text{ cm}^{-1}$  associated with the G and 2D bands, respectively. Interestingly, the Raman spectrum of  $\text{HOPG-ODA}_{\text{LB-eG}}$  displays an additional band at  $1319 \text{ cm}^{-1}$  (D band), which can be assigned to the presence of defects in the  $\text{sp}^2$  lattice, induced by the covalent attachment of ODA on HOPG and  $\text{sp}^2$ -to- $\text{sp}^3$  rehybridization.

The  $I_D/I_G$  integrated intensity ratio of the D and G bands has been shown to be a reliable indicator of the degree of covalent functionalization<sup>39,44</sup>. The  $I_D/I_G$  value obtained for pristine HOPG is equal to 0, indicating the absence of defects while it increases to *ca.* 0.5 after functionalization for HOPG-ODA<sub>LB-eG</sub>, evidencing the formation of covalently attached monolayer of ODA on HOPG.

## Discussion

We report here two different molecular organizations of octadecylamine molecules on HOPG surface. The first one is obtained by physisorption of ODA molecules lying flat on the surface, which spontaneously self-assemble into straight ribbons with chains in parallel alternations. These ribbons are themselves enclosed into HOPG domains of which the different orientations correspond to the hexagonal symmetry of HOPG carbon atoms surface. This supramolecular organization was previously reported for ODA, but also for similar molecules such as N-octadecylacrylamide and N-octadecylcinnamoylamide, which also organize into straight ribbons with a head-to-head arrangement with similar lattice parameters.<sup>45,46</sup>

The second molecular organization (HOPG-ODA<sub>LB-eG</sub>) is new and arises from the original combination of two deposition methods of organic molecules on metallic surfaces: LB transfer and simultaneous oxidative electrografting. We have previously succeeded in the grafting of an ODA LB film onto a gold surface.<sup>42</sup> Here, we have successfully reproduced the same experiment with HOPG, by adapting the experimental parameters during the LB-eG process, particularly the surface pressure for the LB transfer (40 mN/m) and the dipping up speed that was lowered to 0.25 mm/min (4.16  $\mu\text{m/s}$ ) for HOPG. XPS and IR measurements identified the presence of ODA on HOPG, Raman demonstrated its covalent grafting to carbon atoms and AFM revealed the coverage, thickness and discontinuities of ODA monolayer. STM experiments demonstrated that, after the LB-eG process, ODA is ordered inside a crystalline lattice of hexagonal symmetry and of which surface area is 2.5 larger than that of underlying HOPG one (13.74 versus 5.52  $\text{\AA}^2$ ). Note that an ODA Langmuir film spread on water surface at basic pH and compressed at surface pressures 40 mN/m, is organized with predominant hexagonal molecular arrangement of larger surface area ( $S = 19.8 \text{ \AA}^2$ ).<sup>47,48,49,50</sup> The combination of LB transfer and simultaneous electrografting demonstrated the impact of HOPG surface crystalline structure on that of ODA since molecules adopt a hexagonal ordering inside a lattice of smaller surface area than that on water but overlaying 3

carbon hexagons of HOPG surface. This hexagonal symmetry for ODA monolayer after the LB-eG process explains why no domain are detected by STM as observed in the first organization obtained by physisorption.

The presence of circular nanoholes representing 6% of surface area was systematically observed on all samples and the choice of values of 40 mN/m and 0.25 mm/min represent the best compromise in order to minimize the size and number of these holes in the monolayer. Experiments performed at surface pressures higher than 40 mN/m led to bad results, whatever the dipping speed, as discontinuous and heterogeneous film was observed by AFM on HOPG surface with coexistence of numerous areas covered by mono-, bi- or multilayers as well as uncovered areas. Experiments performed at 40 mN/m surface pressure with higher dipping speeds (0.5 and 1 mm/min) also led to unsatisfactory results, with numerous large circular holes (> 100 nm in diameter), despite the almost absence of uncovered areas. Indeed, the size of holes detected in the ODA monolayer was clearly related to the transfer velocity: the faster the transfer, the higher the diameter and number of holes in the monolayer. We checked by AFM that a pure LB transfer (no electrografting) of ODA on HOPG performed at 40 mN/m surface pressure and 0.25 mm/min (4.16  $\mu\text{m/s}$ ) dipping up speed resulted in the almost absence of ODA film on the hydrophobic HOPG surface. We hypothesize that, during the LB-eG process, the circular holes arise from a partial dewetting of ODA monolayer during the LB transfer on HOPG, similar to that observed in successive LB transfers of phospholipid monolayers on mica<sup>51</sup>. Our results demonstrate that electrochemistry is therefore necessary to cover HOPG surface by grafting the amine while the ODA film is transferred from the air/water interface onto HOPG surface.

The mechanism by which amines are grafted on glassy carbon surfaces involves the formation of an aminyl radical that reacts on the surface<sup>52</sup>, but such radical reactions always lead to multilayered films as discussed above. Many efforts have been devoted to the preparation of monolayers by different methods, all these methods<sup>36,37,38,39</sup> limit the growth of the film by limiting the reactivity of the radicals. These films, even if qualified of monolayers are not always compact.<sup>39</sup>

A similar experiment<sup>53</sup> has been described using a diazonium salts substituted by a long alkyl chain that adsorb flat on the surface of graphene or graphite, these adsorbed molecules are then electrografted. The resulting surface has been carefully characterized by redox probe experiments, Raman spectroscopy that present the expected D-band related to sp<sup>3</sup> carbons, electrical measurements, but the STM images, obtained after electrochemical reduction, show the long chain molecules still lying flat on the surface with a thickness of 0.9 nm (measured

from AFM topographical profiles taken on the holey parts of the Single Layer Graphene,<sup>53</sup> Figure S10) and not grafted and standing up on the surface as claimed by the authors. For C22-phenyl moieties bonded to a  $sp^3$  carbon one expects a height of  $\sim 3.4$  nm for standing up groups. Most likely the adsorbed molecules dimerize by radical-radical coupling.<sup>54</sup>

In the present case, the formation of a monolayer is “by construction” and in addition, it presents a crystalline structure. The above experiments indicate that it is possible to prepare and characterize two different structures for ODA on HOPG. The first one corresponds to an adsorbed weakly bound film where the molecules are lying flat on the surface in an intricate manner; the second one obtained by electrografting a Langmuir-Blodgett film. These two structures correspond, with the same molecule, to two different surface modifications as indicated in the introduction.

Such films also open the way to similar films with chemical reactivity that would be useful for the construction of biosensors where a uniform electron transfer through the film is a condition of efficiency.<sup>34</sup> They can also be useful in organic electronics<sup>55,56</sup> where organic films between two metallic contacts permit the formation of molecular junctions. Finally, they pave the way to graft metallic surfaces with organized films of molecules bearing amine groups, such as antimicrobial peptides for the design of antibacterial surfaces.

## CONCLUSION

The self-organization of physisorbed ODA molecules lying flat on the HOPG surface was compared to that obtained by combining simultaneously the Langmuir-Blodgett transfer of an ODA Langmuir film onto HOPG and oxidative electrografting. The original combination of both surface deposition methods permits to obtain a compact, uniform in thickness, crystalline, strongly bound nanometer thick films of octadecylamine. The monocrystalline structure of HOPG domains strongly impact the ordering of octadecylamine deposited onto it using this process, preserving the hexagonal symmetry into ODA one. Such covalent organic films are of interest for the construction of biosensors in electrochemistry or electronics as well as functionalization of surfaces of biomedical interest.

## EXPERIMENTAL SECTION

*Substrate, chemicals.* Highly oriented pyrolytic graphite (HOPG) and cut Pt/Ir tips for STM experiments were commercially purchased from Goodfellow SARL (Lille, France). ODA and 1-heptanoic acid were obtained from Sigma Aldrich (St Quentin Fallavier, France) and used

as received. Ultrapure water ( $\gamma = 72.5$  mN/m at 21°C, resistivity 18.2 M $\Omega$ .cm) was obtained from Millipore Milli-Q Direct 8 water purification system. HOPG surfaces were meticulously cleaved with tape until obtaining a flat surface without any spike protruding from the surface.

*Equipment.* The Langmuir equipment was a Langmuir trough KSV company (775.75 cm<sup>2</sup>, Biolin Scientific, Finland) enclosed into a Plexiglas box to limit surface contamination. The potentiostat used in the transfer experiments was from a Palm Sens 3. All the other experiments were performed with a Versastat 4 potentiostat/galvanostat/EIS from Princeton Applied Research analyzer with VersaStudio software.

*Formation of a Langmuir-Blodgett film and simultaneous electrografting (LB-eG) to HOPG surface.* A spreading organic solution was prepared by dissolving ODA (FW = 269.51 g/mol) in chloroform with a 3  $\mu$ mol/mL concentration. The subphase was ultrapure water maintained at 21°C. Its pH was  $9 \pm 0.2$ , adjusted with a NaOH solution. Before depositing organic solution, the HOPG substrate was previously immersed in the subphase and connected with the potentiostat. Prior to monolayer spreading, the subphase surface was cleaned by suction. Organic solutions of ODA were spread onto water. The waiting time to allow a complete evaporation of the spreading solvent was 15 min before compression was started. The monolayer was compressed continuously at a constant rate of 5 Å<sup>2</sup>.molecule<sup>-1</sup>.min<sup>-1</sup>. The dipping speed and the surface pressure were kept respectively at 0.25 mm.min<sup>-1</sup> and  $40 \pm 0.2$  mN/m. Under these conditions, ODA monolayers were expected to be in a liquid condensed state. The Langmuir trough was equipped with saturated calomel electrode as a reference and carbon paper as counter electrode. Chronoamperometry at  $E = + 0.85$  V/SCE was started simultaneously with the LB transfer and stopped when the HOPG substrate was completely out of the aqueous subphase.

*Atomic Force Microscopy experiments.* AFM experiments were performed using the Nanowizard 3 Ultra Speed from JPK Instruments (Berlin, Germany), installed on an air-buffered table coupled to a dynamic anti-vibration device, and enclosed in an acoustic box. Imaging of organic layers on HOPG substrates was performed in air in AC-HyperDrive® mode, with gold coated silicon cantilevers PPP-NCHAuD of  $40 \pm 10$  N/m spring constant and  $290 \pm 5$  kHz resonance frequency (Nanosensors, Neuchatel, Switzerland). The pyramid-shaped tips had a radius of curvature less than 10 nm. A free amplitude oscillation of 0.8 to 1 nm was chosen allowing a very high resolution of the imaged surface. Images were taken at scan rates of 1 Hz or 0.5 Hz for large scale pictures. Image processing (flatten, plane fit, edge

and hole detection) was performed with the JPK Data Processing software (JPK Instruments). At least three different areas of each sample were scanned, and typical images were presented. Average values of height dimensions of holes were determined with all holes detected in the pictures.

*Scanning Tunneling Microscopy experiments.* ODA molecules were physisorbed onto HOPG from organic solution or electrochemically grafted on a freshly cleaved HOPG substrate using our LB-eG process <sup>37</sup>. 1-heptanoic acid was used as solvents to resolve ODA molecules deposited from organic phase at the solid/liquid interface. STM imaging of the samples was performed at the solid/liquid interface under ambient conditions by a SPM Nanoscope V (Veeco, Bruker) scanning tunneling microscope. Cut Pt/Ir (Goodfellow alloy wire with Pt 80% and Ir 20%) tips were used to obtain constant current images at room temperature with a bias voltage applied to the sample ( $I = 100\text{-}1000\text{ pA}$ ,  $U = -100 \sim -500\text{ mV}$ ). The STM images are processed and analyzed using FabViewer <sup>44</sup> from Fabrication Products.

*Infrared Spectra.* IRRAS spectra of the modified plates were recorded using a purged (low  $\text{CO}_2$ , dry air) Jasco FT/IR-6100 Fourier transform infrared spectrometer equipped with an MCT (mercury-cadmium-telluride) detector. For each spectrum, 1000 scans were accumulated with a spectral resolution of  $4\text{ cm}^{-1}$ . The background recorded before each spectrum was that of a clean substrate.

*XPS Spectra.* XPS measurements were performed using a K-Alpha<sup>+</sup> system (ThermoFisher Scientific, East-Grinstead, UK) fitted with a micro-focused and monochromatic Al  $K\alpha$  X-ray source ( $1486.6\text{ eV}$ , spot size:  $400\text{ }\mu\text{m}$ ). The pass energy was set to 150 and 40 eV for the survey and the high resolution spectra, respectively. The spectra were calibrated against the C—C/C—H C1s component set at 285 eV. The chemical composition was determined by using the manufacturer sensitivity factors using Avantage software, version 5.9902. The spectra were calibrated against C1s set at 285 eV.

*Raman spectroscopy.* Raman measurements were performed using a Horiba XploRA PLUS Raman micro-spectrometer. All the measurements were performed on the HOPG surface, using a laser at 638 nm, an exposition time of 10s and an accumulation of 10 spectra. The scattered light was collected with a long working distance objective of 100 fold magnification (0.9 N.A.).

## Acknowledgment

We are grateful to P. Decorse for the XPS spectra. ANR (Agence Nationale de la Recherche) and CGI (Commissariat à l'Investissement d'Avenir) are gratefully acknowledged for their financial support of this work through Labex SEAM (Science and Engineering for Advanced Materials and devices), ANR-10-LABX-096 and ANR-18-IDEX-00.

## Author information

### N°ORCID

Jérôme Médard : 0000-0002-4167-6336

Xiaonan Sun : 0000-0003-4793-2027

Jean Pinson : 0000-0001-6176-8636

Da Li : 0000-0003-3854-791X

Claire Mangeney : 0000-0002-9817-3262

Jean-Philippe Michel : 0000-0003-0242-2605

---

<sup>1</sup> I. Langmuir, The constitution and fundamental properties of solids and liquids: II. Liquids, *J. Am. Chem. Soc.* 1917, **39**, 1848–1906; G. Roberts, *Langmuir Blodgett Films* (Plenum Press, New York 1990).

<sup>2</sup> D. A. Outka, J. Stöhr, J. Rabe, J. D. Swalen, H. H. Rotermund, Orientation of arachidate chains in Langmuir-Blodgett monolayers on Si(111), *Phys. Rev. Lett.* 1987, **59**, 1321-1324.

<sup>3</sup> J. K. Bal, S. Kundu, S. Hazra, Growth and stability of Langmuir-Blodgett films on OH-, H-, or Br-terminated Si(001), *Phys. Rev. B* 2010, **81**, 045404/1-045404/8.

<sup>4</sup> Y. F. Dufrêne, W. R. Barger, J. B. D. Green, G. U. Lee, Nanometer-Scale Surface Properties of Mixed Phospholipid Monolayers and Bilayers, *Langmuir* 1997, **13**, 4779-4784.

<sup>5</sup> M. Clemente-León, B. Agricole, C. Mingotaud, C. J. Gómez-García, E. Coronado, P. Delhaes, Toward New Organic/Inorganic Superlattices: Keggin Polyoxometalates in Langmuir and Langmuir-Blodgett Films, *Langmuir* 1997, **13**, 2340-2347.

<sup>6</sup> S. Şen,, R. Çapan, Z. Özbek, M. E. Özel, G. A. Stanciu, F. Davis, Langmuir-Blodgett film properties of based on calix[4]resorcinarene and the detection of those against volatile organic compounds, *Applied Physics A* 2019, **125**, 1-11.

<sup>7</sup> C. A. Lang, J. K. H. Hörber, T. W. Hänsch, W. M. Heckl, H. Möhwald, Scanning tunneling microscopy of Langmuir–Blodgett films on graphite, *Journal of Vacuum Science & Technology A* 1988, **6**, 368.

- 
- <sup>8</sup> J. B. Peng, G. T. Barnes, I. R. Gentle, The structures of Langmuir-Blodgett films of fatty acids and their salts, *Advances in Colloid and Interface Science* 2001, **91**, 163-219.
- <sup>9</sup> K. Kojio, A. Takahara, K. Omote, T. Kajiyama, Molecular Aggregation State of n-Octadecyltrichlorosilane Monolayers Prepared by the Langmuir and Chemisorption Methods, *Langmuir* 2000, **16**, 3932-3936.
- <sup>10</sup> J. A. Zasadzinski, R. Viswanathan, L. Madsen, J. Garnaes, D. K. Schwartz, Langmuir Blodgett-Films, *Science* 1994, **263**, 1726-1733.
- <sup>11</sup> J. P. Michel, Y. X. Wang, E. Dé, P. Fontaine, M. Goldmann M., V. Rosilio, Charge and aggregation pattern govern the interaction of plasticins with LPS monolayers mimicking the external leaflet of the outer membrane of Gram-negative bacteria, *Biochim. Biophys. Acta - Biomembranes* 2015, **1848**, 2967-2979.
- <sup>12</sup> J. P. Michel, Y. X. Wang, I. Kiesel, Y. Gerelli, V. Rosilio, Disruption of Asymmetric Lipid Bilayer Models Mimicking the Outer Membrane of Gram-Negative Bacteria by an Active Plasticin, *Langmuir* 2017, **33**, 11028-11039.
- <sup>13</sup> J. J. Benítez, J. A. Heredia-Guerrero, M. A. San-Miguel, H. C. Galloway, Packing Defects in Fatty Amine Self-Assembled Monolayers on Mica as Revealed from AFM Techniques, *J. Phys. Chem. B* 2018, **122**, 493-499.
- <sup>14</sup> S. Uemura, M. Sakata, C. Hirayama, M. Kunitake, Fullerene Adlayers on Various Single-Crystal Metal Surfaces Prepared by Transfer from LB Films, *Langmuir* 2004, **20**, 9198-9201.
- <sup>15</sup> K. S. Mali, J. Adisojoso, E. Gghijens, I. de Cat, S. de Feyter, Exploring the Complexity of Supramolecular Interactions for Patterning at the Liquid-Solid, *Acc. Chem. Res.* 2012, **45**, 1309-1320.
- <sup>16</sup> M. Hibino, Adsorption Behaviors of Mixed Monolayers of n-Alkanes at the Liquid-Solid Interface, *Langmuir* 2016, **32**, 4705-4709.
- <sup>17</sup> F. Silly, S. Ausset, X. Sun, Coexisting Chiral Two-Dimensional Self-Assembled Structures of 1,2,3,4-Tetrahydronaphthalene Molecules: Porous Pinwheel Nanoarchitecture and Close-Packed Herringbone Arrangement, *J. Phys. Chem. C* 2017, **121**, 15288-15293.
- <sup>18</sup> X. Sun, X. Yao, F. Lafolet, G. Lemerrier, J. C. Lacroix, One-Dimensional Double Wires and Two-Dimensional Mobile Grids: Cobalt/Bipyridine Coordination Networks at the Solid/Liquid Interface, *J. Phys. Chem. Lett.* 2019, **10**, 4164-4169.
- <sup>19</sup> X. Sun, F. Silly, F. Maurel, C. Dong, Supramolecular chiral host-guest nanoarchitecture induced by the selective assembly of barbituric acid derivative enantiomers, *Nanotechnology* 2016, **27**, 42LT01.

- 
- <sup>20</sup> H. M. Zhang, Z. X. Xie, B. W. Mao, X. Xu, Self-Assembly of Normal Alkanes on the Au (111) Surfaces, *Chem. Eur. J.* 2004, **10**, 1415-1422.
- <sup>21</sup> R. Yamada, K. Uosaki, Two-Dimensional Crystals of Alkanes Formed on Au(111) Surface in Neat Liquid: Structural Investigation by Scanning Tunneling Microscopy, *J. Phys. Chem. B* 2000, **104**, 6021-6027.
- <sup>22</sup> W. Azzam, P. Cyganik, G. Witte, M. Buck, Ch. Wöll, Pronounced Odd-Even Changes in the Molecular Arrangement and Packing Density of Biphenyl-Based Thiol SAMs: A Combined STM and LEED Study, *Langmuir* 2003, **19**, 8262-8270.
- <sup>23</sup> T. Ishida, W. Mizutani, N. Choi, U. Akiba, M. Fujihira, H. Toku, Structural Effects on Electrical Conduction of Conjugated Molecules Studied by Scanning Tunneling Microscopy, *J. Phys. Chem. B* 2000, **104**, 11680-1168.
- <sup>24</sup> S. P. Pujari, L. Scheres, A. T. M. Marcelis, H. Zuilhof, Covalent surface modification of oxide surfaces, *Angew. Chem., Int. Ed.* 2014, **53**, 6322-6356.
- <sup>25</sup> S. Marcinko, A. Y. Fadeev, Hydrolytic Stability of Organic Monolayers Supported on TiO<sub>2</sub> and ZrO<sub>2</sub>, *Langmuir* 2004, **20**, 2270-2273.
- <sup>26</sup> C. Haensch, S. Hoepfner, U. S. Schubert, Chemical modification of self-assembled silane based monolayers by surface reaction, *Chem.Soc.Rev.* 2010, **39**, 2323-2334.
- <sup>27</sup> K. M. Kallury, R. John, D. Brennan, U. J. Krull, Depth Profiling of Functionalized Silane Films on Quartz and Silicon Substrates and of Urease Immobilized on Such Films by Angle-Resolved X-ray Photoelectron Spectroscopy, *Anal. Chem.* 1995, **67**, 15, 2625-2634.
- <sup>28</sup> P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson, J. M. Savéant, Covalent Modification of Carbon Surfaces by Aryl Radicals Generated from the Electrochemical Reduction of Diazonium Salts, *J. Am. Chem. Soc.* 1997, **119**, 201-207.
- <sup>29</sup> A. Berisha, M. M. Chehimi, J. Pinson, F. I. Podvorica, Electrode surface modification using diazonium salts in Bard, A. J., Zoski, C. G., Eds., *Electroanalytical Chemistry*; 26 CRC Press: Boca Raton, FL, 2016.
- <sup>30</sup> M. M. Chehimi, G. Hallais, T. Matrab, J. Pinson, F. Podvorica, Electro- and Photografting of Carbon or Metal Surfaces by Alkyl Groups, *J. Phys. Chem. C* 2008, **112**, 18559-18565.
- <sup>31</sup> J. Médard, P. Decorse, C. Mangeney, J. Pinson, M. Fagnoni, S. Protti, Simultaneous Photografting of Two Organic Groups on a Gold Surface by using Arylazo Sulfones as Single Precursors, *Langmuir* 2020, **36**, 2786-2793.

- 
- <sup>32</sup> A. Adenier, M. M. Chehimi, I. Gallardo, J. Pinson, N. Vilà, Electrochemical Oxidation of Aliphatic Amines and Their Attachment to Carbon and Metal Surfaces, *Langmuir* 2004, **20**, 8243-8253.
- <sup>33</sup> D. J. Eycken, C. L. Arnold, Ž. Simon, T. R. Gengenbach, J. Pinson, Y. Wickramasingha, L. C. Henderson, Covalent sizing surface modification as a route to improved interfacial adhesion in carbon fibre-epoxy composites, *Composites: Part A* 2021, **140**, 106147.
- <sup>34</sup> D. Hetemi, V. Noël, J. Pinson, Grafting of Diazonium Salts on Surfaces: Application to Biosensors, *Biosensors* 2020, **10**, 4.
- <sup>35</sup> X. Yao, X. Sun, F. Lafolet, J. C. Lacroix, Long-Range Charge Transport in Diazonium-Based Single-Molecule Junctions, *Nano Lett.* 2020, **20**, 6899-6907.
- <sup>36</sup> Y. R. Leroux, H. Fei, J. M. Noël, C. Roux, P. Hapiot, Efficient Covalent Modification of a Carbon Surface: Use of a Silyl Protecting Group To Form an Active Monolayer, *J. Am. Chem. Soc.* 2010, **132**, 14039-14041.
- <sup>37</sup> J. Ghilane, F. Hauquier, J. C. Lacroix, Oxidative and Stepwise Grafting of Dopamine Inner-Sphere Redox Couple onto Electrode Material: Electron Transfer Activation of Dopamine, *Anal. Chem.* 2013, **85**, 11593-11601.
- <sup>38</sup> I. López, S. Dabos-Seignon, T. Breton, Use of Selective Redox Cross-Inhibitors for the Control of Organic Layer Formation Obtained via Diazonium Salt Reduction, *Langmuir* 2019, **35**, 11048-11055.
- <sup>39</sup> J. Greenwood, T. H. Phan, Y. Fujita, Z. Li, O. Ivasenko, W. Vanderlinden, H. Van Gorp, F. Wout, G. Lu, K. Tahara, Y. Tobe, H. Uji-i, S. F. L. Mertens, S. De Feyter, Covalent Modification of Graphene and Graphite Using Diazonium Chemistry: Tunable Grafting and Nanomanipulation, *ACS Nano* 2015, **9**, 5520-5535.
- <sup>40</sup> V. Q. Nguyen, X. Sun, F. Lafolet, J. F. Audibert, F. Miomandre, G. Lemerrier, F. Loiseau, J. C. Lacroix, Unprecedented Self-Organized Monolayer of a Ru(II) Complex by Diazonium Electroreduction, *J. Am. Chem. Soc.* 2016, **138**, 9381-9384.
- <sup>41</sup> N. N. Sergeeva, A. N. Chaika, B. Walls, B. E. Murphy, K. Walshe, D. P. Martin, B. D. O. Richards, G. Jose, K. Fleischer, V. Y. Aristov, O. V. Molodtsova, I. V. Shvets, S. A. Krasnikov, A photochemical approach for a fast and self-limited covalent modification of surface supported graphene with photoactive dyes, *Nanotechnology* 2018, **29**, 275705.
- <sup>42</sup> M. Gabaji, J. Médard, A. Hemmerle, J. Pinson, J. P. Michel, From Langmuir Blodgett to Grafted Films, *Langmuir* 2020, **36**, 2534-2542.

- 
- <sup>43</sup> R. C. Tatar, S. Rabii, Electronic properties of graphite: A unified theoretical study, *Phys. Rev. B* 1982, **25**, 4126.
- <sup>44</sup> Z. Li, H. V. Gorp, P. Walke, T. Hai Phan, Y. Fujita, J. Greenwood, O. Ivasenko, K. Tahara, Y. Tobe, H. Uji-I, S. F. L. Mertens, S. De Feyter, Area-selective passivation of sp<sup>2</sup> carbon surfaces by supramolecular self-assembly, *Nanoscale*, 2017, **9**, 5188-5193.
- <sup>45</sup> P. E. V. Dubrovin, J. W. Gerritsen, J. Zivkovic, I. V. Yaminsky, S. Speller, The effect of underlying octadecylamine monolayer on the DNA conformation on the graphite surface, *Colloids and Surfaces B: Biointerfaces* 2010, **76**, 63-69.
- <sup>46</sup> P. Qian, H. Nanjo, T. Yokoyama, T. Miyashita, T. M. Suzuki, STM observation of N-octadecylacrylamide and N-octadecylcinnamoylamide monolayers self-assembled on a graphite surface, *Chem. Comm.* 1998, **8**, 943-944.
- <sup>47</sup> V. M. Kaganer, H. Mohwald, P. Dutta, Structure and phase transitions in Langmuir monolayers, *Rev. Mod. Phys.* 1999, **71**, 779-818.
- <sup>48</sup> A. Angelova, R. Ionov, Langmuir-Blodgett Film Organization Resulting from Asymmetrical or Partial Types of Monolayer Transfer: Comparison for Amphiphiles of Different Geometrical Shapes, *Langmuir* 1996, **12**, 23, 5643-5653.
- <sup>49</sup> R. Ionov, A. El-Abed, M. Goldmann, P. Perreti, Interactions of lipid monolayers with the natural biopolymer hyaluronic acid, *Biochim Biophysica Acta*. 2004, **1667**, 200-207.
- <sup>50</sup> N. Belman, N. S. Acharya, O. Konovalov, A. Vorobiev, J. Israelachvili, S. Efrima, Y. Golan, Hierarchical Assembly of Ultranarrow Alkylamine-Coated ZnS Nanorods: A Synchrotron Surface X-Ray Diffraction Study, *Nano Lett.* 2008, **8**, 3858-3864.
- <sup>51</sup> P. Bassereau, F. Pincet, Quantitative Analysis of Holes in Supported Bilayers Providing the Adsorption Energy of Surfactants on Solid Substrate, *Langmuir* 1997, **13**, 7003-7007.
- <sup>52</sup> A. Adenier, M. M. Chehimi, I. Gallardo, J. Pinson, J.; Vilà, N.; Electrochemical Oxidation of Aliphatic Amines and Their Attachment to Carbon and Metal Surfaces, *Langmuir* **2004**, **20**, 8243-8253.
- <sup>53</sup> Z. Xia, F. Leonardi, M. Gobbi, Y. Liu, V. Bellani, A. Liscio, A. Kovtun, R. Li, X. Feng, E. Orgiu, P. Samorì, E. Treossi, V. Palermo, Electrochemical Functionalization of Graphene at the Nanoscale with Self-Assembling Diazonium Salts, *ACS Nano* 2016, **10**, 7125-7134.
- <sup>54</sup> B. Cui, J. Y. Gu, T. Chen, H. J. Yan, D. Wang, L. J. Wan, Solution Effect on Diazonium-Modified Au(111): Reactions and Structures, *Langmuir* 2013, **29**, 2955-2960.
- <sup>55</sup> D. D. James, A. Bayat, S. R. Smith, J. C. Lacroix, R. L. McCreery, Nanometric building blocks for robust multifunctional molecular junctions, *Nanoscale Horiz.* 2018, **3**, 45-52.

<sup>56</sup> Q. van Nguyen, P. Martin, D. Frath, M. L. Della Rocca, F. Lafolet, C. Barraud, P. Lafarge, V. Mukundan, D. James, R. L. McCreery, J. C. Lacroix, Control of Rectification in Molecular Junctions: Contact Effects and Molecular Signature. *J. Am. Chem. Soc.* 2017, **139**, 11913-11922.

### Graphical Abstract

