Wet-chemical non-covalent functionalization of CVD-graphene: molecular doping and its effect on electrolyte-gated graphene field-effect transistor characteristics

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Abstract:

Graphene sheets (mono- and multi-layers) were synthesized by chemical vapor deposition and functionalized with various aromatic molecules such as Fe-/Co-porphyrin and Fe-phthalocyanine through π-π interactions. The resulting nano-hybrid materials were characterized by Raman spectroscopy (RS), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and high-angle annular dark-field scanning transmission electron microscopy (STEM-HAADF) techniques. The presence of physi-adsorbed molecules (Fe-/Co-
porphyrin and Fe-phthalocyanine) on the graphene sheet surface is evidenced by spectroscopic and microscopic analysis, which confirm that these molecules are immobilized through electrostatic and π-π interactions. RS confirmed the n- or p-type doping of graphene, according to the chemical nature of those physis-adsorbed molecules. The electrical characteristics of electrolyte-gated graphene field-effect transistors (GFETs) based on nano-hybrid materials were subsequently evaluated and demonstrated a charge transfer between the physis-adsorbed molecules and the graphene. All these results suggest that the electronic structure of graphene can be tailored by doping with aromatic molecules. Density Functional Theory (DFT) calculations were performed to confirm these observations.

**Keywords:** Graphene; Porphyrin; Phthalocyanine; Non-covalent Functionalization; electrolyte-gated GFET.

1. **Introduction**

   Since the isolation of mono- and few-layers graphene, an atomically thin two-dimensional carbonaceous honeycomb, it has become one of the most investigated materials, thanks to its exceptional electrical, mechanical, and chemical properties [1-3]. In particular, the high surface-to-volume ratio, excellent carrier mobility, high thermal conductivity, excellent chemical properties, and unique optical characteristics of graphene make it suitable for a wide range of applications [4]. However, graphene is a semimetal with zero bandgap, which restricts its use in many applications that exploit a semiconducting behavior, such as gas sensing, where an appropriate bandgap is requisite.

   Non-covalent doping has recently emerged as an elegant way to increase graphene's carrier density and adjust its work function [5-7]. Considerable efforts have been made to modify the graphene surface, with organic or inorganic molecules, in order to fabricate graphene nano-hybrid materials for nano-electronic and sensing applications. This effort is motivated by the fact that these hybrid materials combine the unique electrical, optical and
chemical properties of their components and offer the potential to generate synergies from the peculiar properties of each of those components.

Chemical modification of graphene sheets with small organic molecules represents a viable approach for tailoring electronic properties such as band gap opening. Both covalent and non-covalent chemical methods have been investigated for this purpose [8-12]. The latter is particularly promising since the functionalized graphene, through non-covalent functionalization, preserves its π-extended conjugated sp² network.

There is a plethora of aromatic and non-aromatic molecules including, alkyl-amines [13], 7,7,8,8-Tetracyanoquinodimethane [14], pentacene, and phthaloxyanine [15], capable of inducing controllable molecular doping of graphene. The doping process is accompanied by a change in the electronic properties providing thus characteristic signatures, which are essential for sensing applications. Among these molecules, macrocyclic metal complexes with planar structures are excellent candidates for this purpose since they can be easily chemically anchored or physi-adsorbed on the graphene surface through π–π interactions. Furthermore, combining graphene with planar macrocyclic metal complexes provides new functionalities, thanks to the synergy from both components. Consequently, several studies have shown that Por or Phc graphene hybrid photodetectors exhibit enhanced photo- and chemical responses compared to the pristine graphene [16-19].

Regarding the molecular doping and its effect on the electronic properties, non-covalent functionalization of graphene sheets by Por has shown a clear evidence of doping by charge transfer processes, as well as graphene's work function modulation. Using a statistical analysis of scanning tunneling spectroscopy measurements, Arramel et al. [20] demonstrated that the non-covalent interaction of metallic porphyrins with Chemical Vapor Deposition (CVD)-graphene sheets could cause a bandgap opening that could be tuned, by changing the central metal of the porphyrin. Gajarushi et al. [21] investigated the electronic properties of graphene
non-covalently functionalized with porphyrin and its metalled form, zinc-porphyrin. The non-
covalent functionalization of graphene using porphyrin molecules showed a positive shift of
the transfer curve and Dirac point in graphene field-effect transistors (GFETs), enhanced hole
current, and reduced electron current. When implemented in chemiresistive sensor, many \textit{Por}
molecules show strong dipoles once bound to an analyte and relatively weak dipoles in their
unbound states. These strong dipole interactions alter the carrier concentration in the underlying
graphene and ultimately modulate the sensor conductivity based on analyte concentration [22].

Pyo \textit{et al.} [23] reported a highly sensitive, flexible and transparent UV detection and vapor
toluene sensing chemiresistor based on CVD graphene functionalized with \textit{Por} via one-step
evaporation. Co porphyrin was deposited on the graphene by thermal evaporation. To
investigate the influence of Co porphyrin functionalization on the electronic properties of
graphene, they fabricated a field-effect transistor. The electrical measurements revealed that
sensors were n-doped, and their resistance decreased upon exposure to toluene. Swager and co-
workers [22] fabricated a highly sensitive ammonia gas chemiresistor based on Co porphyrin
functionalized graphene CVD. The gas chemiresistor device was fabricated by drop-casting a
porphyrin solution on a CVD-graphene sensor array. Porphyrin-functionalized graphene
exhibited enhanced ammonia sensitivity compared to pristine graphene.

In most cases, when organic molecules are used to functionalize the graphene surface,
they are deposited on graphene sheets by vapor-phase and form island structures. However, to
realize low-cost fabrication processes for organic-graphene hybrid electronics, physical vapor
deposition methods are not compatible with low-cost products (plastic substrates). Wet-
chemical non-covalent functionalization of graphene with small molecules offers a simple and
economical way to produce large quantities of hybrid materials with many functionalities, using
low-cost equipment. Moreover, chemically functionalized 2D materials possess a high potential
for developing novel functional devices for new applications. Although the molecular
functionalization of graphene with monolayers that can serve as dopants is well established, new advanced characterization techniques that can be used for nano-hybrid structured materials are not extensively developed.

This work combines several experimental characterization methods with theoretical calculations to develop a deep understanding of the interaction and the influence of Por and Phc on the electronic properties of CVD graphene sheets. MPo and MPc molecules were chosen because their aromatic backbone promotes non-covalent bonding with the graphene plane, and they have strong dipoles when interacting with specific gas analytes, making them good candidates for the fabrication of selective graphene gas-detecting materials. The functionalization with Fe-porphyrin, Co-porphyrin, and Fe-phthalocyanine was carried out using a drop-casting method. The graphene sheets were synthesized by CVD on high purity copper foils [24]. These metallo-aromatic molecules form a stable adsorbed layer attached to the surface of graphene. A partial electron transfer between graphene and molecular adsorbed layer results in p-type or n-type doping of the graphene depending on the type of the molecules and the metal of the complexes. These results are confirmed by Raman spectroscopy, energy dispersive spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, and transmission electron microscopy.

The charge transport studies were performed using electrolyte-gated GFET devices in ambient air to probe the change in the electrical properties of Por/Phc graphene nanohybrid materials and Por/Phc and to confirm graphene's doping effect. A theoretical approach is developed to evaluate the charge transfer between the metal-centered molecules and graphene.

2. Material and methods

2.1. Synthesis of graphene

Single-layer graphene was synthesized by thermal CVD on high purity copper foils (Goodfellow Cu000410: 99,99+% purity, 0.025 mm thick), according to the process published previously [24]. Briefly, the copper foil is cut into 10 cm × 10 cm parts and fit into a graphite
confinement box which isolates the substrate from sources of contamination. The substrate is introduced into a three-zone quartz tube furnace (EasyTube ET3000, CVD Corp.) and first annealed at 1020 °C for 20 min in a hydrogen atmosphere (300 sccm, 0.5 Torr). The gaseous carbon source is a mixture of methane and hydrogen (H₂:CH₄ 6:1, 0.5 torr) that flows into the furnace for 30 min while keeping the temperature at 1020 °C. The transfer is performed by plasma etching the graphene from one of the sides of the copper sheet and spin-coating a poly(methyl methacrylate) (PMMA) support layer on the graphene on the other side (1600 RPM dried vertically overnight at 20 °C). Then the Cu foil is dissolved in 0.48 M FeCl₃ at 35 °C for 30 min, followed by rinsing in 3 cycles of chemical baths (per cycle: 5min in water; 30min in 2% HCl, v/v) and manual transfer onto a 200 mm oxidized p-type silicon wafer. The PMMA layer is finally dissolved (sample dipped in acetone overnight, followed by a two-hours, 300 °C bake).

2.2. Functionalization of graphene sheets

All reagents (5,10,15,20-Tetraphenyl-21H,23H-porphine iron (III) chloride (Fe-Por) (94%), 5,10,15,20-Tetraphenyl-21H,23H-porphine cobalt(II) (Co-Por) (85%) and iron (II) phthalocyanine (Fe-Phc)) (90%), as well as organic solvents (dichloromethane (DCM)) and acetone) were purchased from "Merck". The reagents were used without further purification. The functionalization of the graphene was achieved following our previously published procedures [25]. The Por or Phc compounds were dissolved in DCM at a 5.10⁻³ mol/l Fe-Por concentration, a 10⁻⁴ mol/l Co-Por concentration, or a 5.10⁻⁴ mol/l Fe-Phc concentration. 10 µl of Por or Phc solution was drop-cast onto the surface of a graphene sheet. After rinsing several times with acetone to remove the excess of unbound molecules, the functionalized graphene (Fe-Por-graphene, Co-Por-graphene, or Fe-Phc-graphene) was then dried at 40 °C for 5 min.

2.3. Characterization methods
Different techniques were used to characterize the structure, microstructure, and composition of nano-hybrid materials. The efficiency of the physi-adsorption process was first evaluated by Raman spectroscopy. The morphology of the nano-hybrid materials was microscopically analyzed using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The chemical properties and elemental composition of nano-hybrid materials were characterized by Energy Dispersive Spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The transport studies were performed using electrolyte-gated GFET devices in ambient air. The theoretical density functional theory calculations (DFT) (open-shell) were carried out using the CRYSTAL17 code.

2.3.1. Raman spectroscopy. Raman spectra were recorded using a high-resolution confocal Raman microscope (Labram HR800; HORIBA Jobin Yvon France) through a 100× microscope objective (NA=1) to demonstrate the presence of porphyrin and phthalocyanine after functionalization. Micro-Raman mapping was performed in high-resolution mode, using laser excitation of λ=532 nm with 20s acquisition time and two accumulations per spectrum. The number of gratings in the Raman spectrometer was 600 grooves per mm. Raman mapping was performed on 5 µm × 5 µm areas with a step size of 0.2 µm.

2.3.2. Scanning Electron Microscopy. Scanning Electron Microscopy (SEM) observations were carried out using HITACHI S 4800 electron microscope. Further, to investigate the chemical state of the functionalized graphene, energy dispersive spectroscopy (EDS) analyses (Thermo Ultra Dry) were performed.

2.3.3. High Resolution-Transmission Electron Microscopy and Scanning Transmission Electron Microscopy. The High Resolution-Transmission Electron Microscopy (HR-TEM) analyses were performed using a Thermo Fisher Titan-Themis electron microscope operating at 80 and 300kV. For the graphene characterization (before and after functionalization), an operating voltage of 80 kV was used to avoid any beam damage. Before the TEM observations,
a preliminary step was mandatory, consisting of transferring the graphene from the substrate surface onto Cu-mesh TEM grids. This has been done using a polymethyl methacrylate (PMMA) transfer method [26]. The PMMA was spin-coated onto the Si/SiO₂-graphene at 3000 rpm for 40 s, followed by drying at 100°C for 5min. Then, the Si/SiO₂ was etched in NaOH (1mol/l) for one hour. The graphene/PMMA was removed and placed into deionized (DI) water baths. After rinsing several times with DI water, the PMMA/graphene assembly was carefully deposited onto the TEM grid. Finally, the TEM grids were dried at 100°C for 24h, and then the PMMA was dissolved in acetone. The molecules (Por or Phc) were deposited by a drop-casting of a 10µL drop of a solution (Por or Phc) in DCM directly on top of the graphene surface, followed by a thorough acetone washing process of non-grafted molecules. In order to probe the presence of Por element components (Fe or Co) or Phc (Fe) chemical state, energy dispersive spectroscopy (EDS) analyses have been performed on a 200kV Titan-Themis TEM/STEM electron microscope equipped with a Cs probe corrector and a Chemistem Super-X detector. These two accessories allow chemical mapping of the light and heavy elements with a spatial resolution in the picometer range. To avoid sample damage during the Scanning Transmission Electron Microscopy (STEM)-HAADF chemical analysis, the acquisition conditions have been slightly modified to use a very low beam current.

2.3.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) measures were performed using an XPS KRATOS, analytical AXIS UltraDLD spectrometer Thermo Scientific KAlpha XPS system (UK). The monochromatized Aluminium-Kα X-ray source (hν = 1486.6 eV) was set-up via an electromagnetic lens mode and in a constant analyser energy mode (CAE = 150 eV for survey spectra and CAE = 30 eV for high resolution spectra). The binding energy scale was initially calibrated using the Ag 3d5/2 (368.2 eV), Cu 2p3/2 (932.7 eV) and Au 4f7/2 (84 eV) peak positions. In addition, the C 1 s hydrocarbon (285.0 eV) binding energy (BE) was used as an
internal reference for calibration. Simulation and quantification of the experimental peaks were performed using the Casa XPS and Origin softwares. Moreover, quantification took into account a nonlinear Shirley background subtraction [27].

2.3.5. Charge transport studies.

A detailed account of the fabrication procedure for GFETs, following the method of a transfer assisted by a metallic sacrificial layer, is described elsewhere [28] and briefly given below:

**GFET fabrication:** A back-gate access is first prepared by lithography and reactive ion etching on a 200 mm silicon wafer (p-doped, Si-mat) covered with 100 nm of thermal oxide. A thin metal film (Cr 3 nm / Au 30 nm / Al2O3 20 nm) is deposited and patterned into contacts by optical lithography and ion milling performed at 40° from normal incidence. A sacrificial layer (TiWN 5 nm / Al 100 nm / TiWN 15 nm) is deposited, by lift-off, on the wafer excepted the place of the graphene channel. Graphene is transferred by the wet technique explained above and patterned by ICP (1200 W, O2 100 sccm, 0.03 mbar, 30 s). The sacrificial layer is removed by wet etch steps (H2O2 30% 150 s, AZ400K 1:4 240 s, H2O2 30% 50 s). A stopping layer consisting of Cu 10 nm / AlSiCu 30 nm / TiWN 15 nm is sputtered onto the graphene channel and patterned by lift-off into gate electrode and contact pads. A silicon oxynitride passivation is then grown by PECVD onto the wafer. It is patterned and etched in reactive ion etching down to the stopping layer, which is then removed by wet etch, finalizing the device.

**GFET to probe doping of graphene:** Electrolyte-gated GFET was used to probe the doping of graphene. In such a device structure, a droplet of deionized water was used as an electrolyte. The electrical characteristics of electrolyte-gated GFETs were measured using a semiconductor parametric analyzer Keithley 4200-SCS under ambient conditions by applying a source-drain voltage (V_DS = 1 mV) and measuring the source-drain current (I_DS) as a function of the source-gate voltage (V_GS).
**GFET Functionalization:** The functionalization was carried out by drop-casting 10 µl of a solution of molecules (Fe-Por or Co-Por or Fe-Phc in DCM) on the GFETs surface followed by a drying step (1h at 40°C). The device was then thoroughly rinsed several times with acetone to remove unbound molecules.

### 3. Results and discussion

Raman spectroscopy is a powerful non-destructive tool to characterize carbonaceous materials, particularly for distinguishing ordered and disordered crystal structures of carbon. Moreover, it has been widely used to reveal the number of stacked graphene layers and distinguish the n- and p-type doped graphene resulting from band shifts [7]. Interaction between graphene and Fe-Por-graphene, Co-Por-graphene, and Fe-Phc-graphene in the nanohybrid materials was first studied by Raman spectroscopy. Figure 1 shows the Raman spectra of graphene, Fe-Por-graphene, Co-Por-graphene, and Fe-Phc-graphene. All Raman spectra were recorded at an excitation wavelength of 532 nm under ambient conditions. The Raman spectra display three bands; a weak D band at ~1350 cm⁻¹ corresponding to defect-induced zone boundary phonons, a strong G band at ~1585 cm⁻¹ characteristic of in-plane optical mode of sp²-hybridized carbon, and a broad 2D band at ca. ~2695 cm⁻¹ attributed to two-phonon double resonance process [29, 30]. The characterization at different areas at the edge and the central region of several samples shows that the graphene film contains a mixture of monolayer and few-layer graphene flakes (see Figure 1(a) and Figure 1(b)). By comparing pristine (unfunctionalized) and functionalized graphene, new peaks appeared in the latter, between 1050 and 3000 cm⁻¹, which probably reveals the presence of physi-adsorbed molecules. The surface of silicon substrates was functionalized with Fe-porphyrin, Co-porphyrin, and Fe-phthalocyanine following the same process and then analyzed with Raman spectroscopy (see Figure S1 in the supporting information (SI)) to confirm this hypothesis. The resulting mapping shows several peaks between 1000-3000 cm⁻¹ that are identical or close to those previously
observed on functionalized graphene. Figure 1 shows that these bands are characteristics of the physi-adsorbed molecules (see Figure S1). Moreover, a decrease of $I_{2D}/I_G$ (the 2D band intensity divided by G band intensity) was also observed. Indeed, the $I_{2D}/I_G$ ratios are $1.694 \pm 0.005$ for graphene, $0.892 \pm 0.025$ for Co-Por-Graphene, $0.765 \pm 0.005$ for Fe-Phc-Graphene, and $0.623 \pm 0.018$ for Fe-Por-Graphene. These measurements were obtained from 45 spectra taken on different zones on each sample. All these confirm that these aromatic molecules cause an apparent decrease in $I_{2D}/I_G$, which can be ascribed to graphene doping [7, 31-32]. The above results can be explained by the fact that all these molecules possess a large aromatic system, which helps to form a stable adsorbed layer on the surface of graphene through n-$\pi$ interactions. As reported in [33], These n-$\pi$ interactions are favorable for the charge transfer between porphyrins and phthalocyanines and the graphene. Therefore, the ratios of the D to the G band changes only slightly (Fe-Por-graphene (~ 0.75), Co-Por-graphene (~0.72), Fe-Phc-graphene (~ 0.70) and graphene (~ 0.76)), from 0.7 to 0.76 after functionalization, confirming that the functionalization does not destroy the extended $\pi$-conjugation system of the graphene [34]. Furthermore, the Raman data show a single 2D Lorentzian peak (ca. $2700 \text{cm}^{-1}$) before and after functionalization, consistent with an unperturbed $\pi$ band, indicating that graphene's fundamental structural properties remain intact after its non-covalent chemical functionalization with Fe-porphyrin, Co-porphyrin, and Fe-phthalocyanine [35-36].

The doping of aromatic molecules on graphene decreases the intensity ratio of $I_{2D}/I_G$ and affects the Raman frequencies of pristine graphene. Upon n- or p-type doping, the 2D peak position, Pos (2D), shifts from its initial position to higher wavenumbers. However, the G band position, Pos(G), shifts upwards with the p-type doping and vice-versa shifts downwards with the n-type doping [5, 7]. To obtain quantitative analysis of the doping effect of graphene with aromatic molecules, multiple measurements were carried at different zone on each sample. Therefore, a large number of Raman spectra (5 maps, each one containing 120 spectra) were
collected on each sample before and after functionalization. Figure 2 presents Pos (2D) versus Pos (G) for pristine graphene, Fe-Por-graphene, Co-Por-graphene, and Fe-Phc-graphene. As indicated from the statistical results of figure 2, Pos (2D) and Pos (G) are shifted after functionalization by Fe-porphyrin, Co-porphyrin, and Fe-phthalocyanine. Indeed, Pos (G) is upshifted for Fe-Phc-graphene, thus indicating that Fe-Phc have induced p-type doping (decreasing electron concentration) in pristine graphene. On the contrary, Pos (G) is downshifted for Fe-Por-graphene and Co-Por-graphene, which suggests that Fe-Por and Co-Por molecules cause n-type doping (increasing electron concentration) in the graphene. This frequency shift is compatible with a doping-induced change of the Fermi energy and consistent with a charge transfer between the graphene and aromatic molecules [5, 7, 31, 37]. On one hand the Raman spectroscopy confirms that the Fe-porphyrin, Co-porphyrin, and Fe-phthalocyanines molecules remain at the graphene surface despite intensive washing with acetone. On the other hand, these results demonstrate an effective charge transfer effect from Por and Phc to the graphene while suggesting the non-covalent interaction of these molecules and graphene.
Figure 1. Raman spectra of (top to bottom) graphene monolayer, graphene multi-layers, Fe-Por-graphene, Fe-Phc-graphene, and Co-Por-graphene. ($\lambda_{exc}=532$ nm).
Figure 2. Position of the Raman 2D peak (Pos (2D)) versus position of the Raman G peak (Pos (G)) of graphene before and after functionalization with Fe-Por, Co-Por and Fe-Phc via drop-coating.

The morphology and the structure of graphene, Fe-Por-graphene, Co-Por-graphene, and Fe-Phc-graphene were further investigated by SEM and TEM analysis. SEM analysis was utilized to characterize the microstructure of the graphene and functionalized graphene on silicon substrates. Typical SEM images of functionalized graphene are displayed in Figure 3. As shown in Fig. 3(a), Fig. 3(c), and Fig. 3(e), functionalized graphene exhibits a layered structure, with a wrinkled surface. The functionalization does not cause significant changes in the graphene flakes structure. Some aggregates with different sizes were observed in some areas on the functionalized surfaces (see Figure S2). To determine their chemical composition, we performed element mapping using the EDS technique, which indicates the presence of Fe and Co elements but in small quantities (Figure 3(b), 3(d), and 3(f)), suggesting again that the porphyrins and phthalocyanines are physi-adsorbed onto the graphene sheets.
Figure 3. SEM images of graphene (a) and functionalized graphene with Fe-Phc (e), Co-Por (f), and Fe-Por (g). Energy-dispersive X-ray analysis (EDS) spectra of graphene (b) and Fe-Por-graphene (d), Co-Por-graphene (f), and Fe-Phc-graphene (h).
The TEM and STEM analysis further confirmed the formation of the as-prepared nanohybrids. Figure 4(a) displays TEM images of graphene after transfer onto the TEM holey carbon grid. TEM images of graphene layers were obtained for all samples. Furthermore, according to the TEM observations, the graphene flakes appear relatively thin and transparent. More TEM images of pristine graphene are shown in figure S3 in supporting information. The corresponding electron diffraction pattern of the chosen area (the inset of Figure 4(a)) indicates the crystalline structure of the graphene sheet with some amorphous part, which is most probably due to the transfer process where the PMMA polymer has not been completely removed.

Figure 4(b) shows Fe-Por aggregates with different sizes (the areas marked by the yellow circle). Regarding the functionalized graphene, some TEM images of the Fe-Por graphene hybrid structure are shown in Figure 4(c), Figure 4(d), and Figure S4 (SI) showing a relatively large and transparent graphene sheet with the presence of some small aggregates (the area marked with arrow) on the graphene surface. Similar results were also observed for Co-Por-graphene, and Fe-Phc-graphene, respectively (see Figure S5 and S6 in SI).
Figure 4. TEM observations of graphene before and after functionalization with Fe-Por. (a) TEM image of a pristine graphene sheet. (b) STEM-HAADF image of Fe-Por. (c-d) HR-TEM image of functionalized graphene with Fe-Por.

To complete the SEM and TEM observations and to get more insight into the non-covalent functionalization of Fe-Por-graphene hybrid structure, chemical analyses using the energy-dispersive X-ray spectroscopy technique in the scanning transmission electron microscopy- high angle annular dark field (STEM-HAADF-EDS) mode of the electron microscope have been performed on different areas of the sample. This type of analysis enables better identification of the presence of the Fe-Por on the top of the graphene structure. As elements of interest, we have chosen the K edges of Carbon (C) at 0.27 eV, Nitrogen (N) at 0.39 eV, and Iron (Fe) at 6.408 eV.
Figure 5 displays STEM-EDS line scan analyses recorded on a chosen area on the surface of Fe-Por-graphene. From Figure 5, we can identify the elemental signal of Fe and N, suggesting the presence of Fe-Por on the surface of graphene. From the STEM-HAADF image illustrated in figure 5(a), a chemical image where the intensity is directly related to the atomic number, the Fe presence is difficult to identify within the aggregate. However, from the STEM-HAADF EDS line scan spectra recorded along the yellow arrow in the image, the Fe presence in a small amount can be observed. More similar analyses on different areas within the same sample are illustrated in Figure S7 and Figure S8 in SI. Similar results were also obtained for Co-Por-graphene and Fe-Phc-graphene and are presented in Figure S9, S10, S11, and S12 in SI.

![Figure 5](image)

**Figure 5.** STEM-HAADF-EDS line scan analyses of Fe-Por functionalized graphene: (a) STEM-HAADF micrograph on the chosen area where a line scan along the direction indicated by the yellow arrow was performed. (b) Corresponding STEM-EDS line scan spectrum showing the variation of the Nitrogen (in blue), Iron (in orange), Carbon (in black) and Oxygen (in green) signal recorded along the scanning direction indicated by the green arrow in (c). (c) Zoom of the analyzed area indicated by the yellow arrow in (a).

X-ray Photoelectron Spectroscopy (XPS) technique has been used in order to corroborate the STEM-HAADF-EDS analyses and to characterize the chemical composition and state of elements present in the investigated nano-hybrid materials. Figure 6 displays the survey spectra of as-prepared nano-hybrids materials. It can be seen that only four peaks corresponding to Si2s, Si2p, C1s, and O1s elements were detected in the spectrum of graphene (Figure 6(a)), originated from SiO2/Si substrate and graphene. However, after functionalization
with Fe-Phc, two additional peaks can be observed, characteristic of Fe and N, suggesting the successful grafting of phthalocyanines onto the graphene surface. Similar results were also obtained for Fe-Por-graphene and Co-Por-graphene presented in Figure S13, Figure S14, Table S1 and Table S2. After graphene functionalization with Fe-Phc, Fe and N elements are detected, and their content is 0.3% and 1.3%, respectively. Since graphene does not contain Fe and N but Fe-Phc does, it can be said that the Fe and N elements in Fe-Phc-graphene originate from Fe-Phc, indicating that Fe-Phc is physi-adsorbed on the surface of the graphene to form a nanohybrid material.

Furthermore, to investigate the chemical states of elements, narrow scans were performed on the C1s, N1s, and F2p. The high-resolution C1s spectra of graphene and Fe-Phc-graphene are shown in Figures 7(a) and 7(b), respectively. The deconvolution of the experimental spectra was made with a Gaussian-Lorentzian shape. As shown in Figure 7(a), the deconvolution of the C1s peak of pristine graphene exhibits three peaks centered at binding energies of 284.8, 286.5, and 288.5 eV, which can be assigned to the C=C/C=C/C-H, C-O/C=C=OH, and OH-C=O bonds, respectively [38]. In Fig. 7(b), the C1s XPS spectrum of Fe-Phc-graphene at around 286 eV indicates C-N and C=N, in agreement with N1s spectrum, explained below, implying that Fe-Phc moieties were successfully adsorbed on the graphene sheets.

Figure 7 (c) displays the high-resolution N1s spectrum for the as-prepared sample, which after deconvolution shows three main peaks at 398.5, 399.6, and 401.4 eV attributed to N=C, N-C, and *NR4, respectively. The content of the N element in Fe-Phc-graphene is 1.3%. The Fe2p spectra (Figure 7(d)) shows two peaks at 710.3 eV and 724.7 eV, which are characteristic of Fe2p3/2 and Fe2p1/2, respectively. Both N1s and Fe2p spectra present direct evidence of the successful functionalization of graphene with Fe-Phc. To summarize at this point, the various results obtained by spectroscopic and microscopic techniques have demonstrated that there are π-π electron interactions and an effective charge transfer between
porphyrins or phthalocyanines and graphene. These results suggest that the functionalization of graphene with different Por or Phc is a promising approach to develop new materials which could be used in a new generation of gas sensors.
**Figure 6.** XPS spectra of pristine graphene and Fe-Phc-graphene.

![Figure 6](image)

**Figure 7.** The XPS spectra of C1s of pristine graphene (a) and Fe-Phc-graphene (b). (c) The XPS spectra of N1s of Fe-Phc-graphene. (d) The XPS spectra of Fe2p of Fe-Phc-graphene.

![Figure 7](image)

To analyze the non-covalent doping graphene mechanism by Co-Por molecule, periodic unrestricted DFT calculations were carried out using CRYSTAL17 package [39]. The graphene has been widely studied and previous theoretical works indicate that PBE functional is widely used in graphene studies [40-42]. The calculated bond length of graphene equals to 1.429 Å
which corresponds to lattice parameter $a = 2.475 \ \text{Å}$. This value is in agreement with the experimental value of $1.420 \ \text{Å}$ [43].

The adsorption of Co-Por molecule on the surface of the graphene is mainly described by the interaction between the metal center (cobalt (II)) and a C-C bond of graphene (see Figures 8(a) and 8(b)). The computed binding energy is $E_b = -180.67 \ \text{kJ.mol}^{-1}$. To the best of our knowledge, there is no former information in the literature to compare with this value, but Touzeau et al. reported a value of $-151.04 \ \text{kJ.mol}^{-1}$ for the adsorption of Fe-Por on graphene [44].

The variation of Fermi levels with the addition of Co-Por molecule on the graphene surface is presented in Figure 8(c). The Fermi level, $E_f$, is increased with the functionalization of graphene surface, with $E_f - E_f(\text{graphene}) = 0.1233 \ \text{eV}$, indicating that Co-Por is electron donor. This result is confirmed by the net charge transfer ($\Delta q$) from Mulliken analysis giving $\Delta q(\text{graphene}) = -0.0789475e$ after functionalization. Thus, the semimetal graphene is n-type doped by the functionalizing molecule. These results are in line with the experimental results.
Figure 8. Optimized geometry of the Co-Por adsorbed on the graphene. (a) front view, (b) top view and (c) fermi levels of graphene pristine and graphene_Co-Por at the PBE-D3/6-31G** level of theory using CRYSTAL.

Electrical characterizations were performed to confirm on the one hand the successful formation of nano-hybrid materials and, on the other hand, to investigate the influence of the functionalization on the electronic properties of graphene. The charge transport studies were carried out using electrolyte-gated GFET devices under ambient conditions. The inset of Figure 9(a) and Figure S15 shows a schematic illustration of an electrolyte gated field-effect transistor consisting of a graphene sheet as the channel, on top of a SiO$_2$/Si substrate (a 200 nm thick SiO$_2$ film and a 725 µm thick doped Si (100) wafer), a gold electrode on the top of the SiO$_2$/Si substrate. A droplet of deionized water is used as the gate dielectric. Figure S16 presents an SEM image of the GFET before functionalization. The measurements were carried out with a drain-source bias of 1 mV, and a gate voltage sweep from 0 to 1V in steps of 0.02 V. Figure
9(a) shows the current-voltage ($I_{DS}$-$V_{GS}$) curves of the graphene transistor before functionalization. The ($I_{DS}$-$V_{GS}$) curve of graphene shows the typical ambipolar character of GFET, i.e., the curve is symmetric around the minimum of $I_{DS}$, which is called $V_{Dirac}$ or Dirac point (corresponding to the channel conductance minimum). It also shows that, due to the fabrication processing, our graphene is initially p-type doped with the Dirac point found at positive $V_{GS}$ values. The transfer curve was repeated several times (5-10 times) to obtain a stable position before functionalization (see Figure 9(a)). To reveal the doping effect of various aromatic molecules, we examined the shift of the Dirac point, which is directly related to the Fermi energy change in the graphene. The $I_{DS}$-$V_{GS}$ curves for functionalized graphene with Co-Por, Fe-Por, and Fe-Phc are presented in Figures 9(b), 9(c), and 9(d), respectively. In Figures 9(b) and 9(c), the Dirac point is downshifted, thus indicating that Co-Por and Fe-Por are causing n-type doping of graphene and suggest an electron transfer from these molecules to graphene. This behavior has been observed consistently in various devices prepared under the same conditions (see Figure S17 and S18 in supporting information). The work function difference between graphene and these compounds explains this behavior when the compounds are deposited on the graphene surface. The Fermi energy levels align by charge transfer from Co-Por or Fe-Por to graphene through the interface between them, inducing n-type doping [23, 45]. However, the transfer curves of functionalized graphene with Fe-Phc show a positive shift in the Dirac point (see Figure 9(d)), suggesting a hole doping of graphene. The statistical results confirm this behavior (Figure S19 in supporting information).

Electrical characterizations evidence that the graphene is successfully functionalized with Por and Phc and a charge transfer between the compound molecules and graphene occurs, confirming the non-covalent functionalization of graphene. Therefore, it is concluded that the Co-Por and Fe-Por cause n-type doping while Fe-Phc imposes p-type doping on graphene. These results are in good agreement with earlier ones of graphene non-covalently functionalized
with porphyrins and phthalocyanines [23, 45]. Finally, Raman and transport experiments converge on the charge transfer signal between graphene and the aromatic molecules.

The presence of Fe, Co, and N revealed by EDS and XPS analysis, the shift of G and 2D bands observed in Raman spectra, and the shift of the Dirac point after graphene functionalization all indicate the successful non-covalent functionalization of graphene and the electron transfer process between the physi-adsorbed molecules and graphene. Therefore, Por and Phc can modulate the doping level or the Fermi energy of graphene.

![Graphene field-effect transistor transfer characteristics](image)

**Figure 9.** Transfer characteristics of graphene field-effect transistors before and after functionalization with Por and Phc. (a-d) Drain current vs. gate voltage characteristics of as-fabricated electrolyte-gated GFET (a) and functionalized GFET with Co-Por (b), Fe-Por (c), and (d) Fe-Phc. The Dirac point is shifted after functionalization in all cases. The dotted lines in (b-d) indicate the position of $V_{\text{Dirac}}$ before functionalization.

4. **Conclusion**
Graphene nano-hybrid materials have been successfully prepared through a facile and straightforward process. The presence of Fe-Por, Co-Por, and Fe-Phc in the nano-hybrid materials was confirmed by EDS and XPS analysis. The non-covalent functionalization and the charge transfer between graphene and physi-adsorbed molecules were evidenced by Raman spectroscopy and electrical characterizations. SEM and TEM images evidenced the morphologies of nano-hybrid materials. Considering the remarkable properties of graphene and MPo or MPc, these nano-hybrids materials might have potential applications in large-area electronics, such as sensors, solar cells, and nano-electronics. The application of these nanomaterials to explore their unique properties is underway in our group.

**CRediT authorship contribution statement**

F. Bouanis, A. Yassar, D. Pribat, J. Borme, P. Alpuim and C. Leonard planned and conceived the experiments and studies. C. M. Abreu, J. Borme and P. Alpuim synthesized the graphene and prepared electrolyte-gated GFETs. F.B. and M.D. prepared and characterized the surface by Raman Spectroscopy and SEM-EDX. F.B., M.D. and I. F. prepared and performed the HR-TEM-STEM studies. F.B, M.D. and C.J. prepared and performed XPS studies. F.B. and M.D. prepared the devices and performed the transport studies. C.L. and M.B. carried out the theoretical studies. All authors contributed to the analysis of the different studies. F.B. wrote the paper with contributions from all the authors.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have or could be perceived to have influenced the work reported in this article.

Supporting Information. Brief descriptions in nonsentence format listing the contents of the files supplied as Supporting Information.

References:


