Non-Covalent functionalization of Single Walled Carbon Nanotubes with Fe-/Co-porphyrin and Cophthalocyanine for Field-Effect Transistor Applications

Fatima Bouanis^{1,2*}, Mohamed Bensifia³, Ileana Florea², Samia Mahouche-chergui⁴, Benjamin Carbonnier⁴, Daniel Grande⁴, Céline Léonard³, Abderrahim Yassar², Didier Pribat²

¹COSYS-LISIS, Univ Gustave Eiffel, IFSTTAR, F-77454 Marne-la-Vallée, France

²Laboratory of Physics of Interfaces and Thin Films, UMR 7647 CNRS/ Ecole Polytechnique, IPParis, 91128 Palaiseau-France.

³MSME, Univ Gustave Eiffel, CNRS UMR 8208, Univ Paris Est Creteil, F-77454 Marne-la-Vallée, France

⁴ Univ Paris Est Creteil, CNRS, ICMPE, UMR 7182, 2 rue Henri Dunant, 94320 Thiais

Supporting information

I. Raman spectroscopy.



* **Corresponding author at:** Univ Gustave Eiffel, IFSTTAR, F-77454 Marne-la-Vallée, France

Tel: +33 (0) 1 69 33 43 85, E-mail address: fatima.bouanis@ifsttar.fr (Fatima Zahra Bouanis)

Figure S1. Raman radial breathing mode (RBM) spectra before (a) and after functionalization (b) with Co-Po.



Figure S2. Raman radial breathing mode (RBM) spectra before (a) and after functionalization (b) with Co-Phc.



Figure S3. The Raman mapping of an oxidized silicon substrate functionalized with Fe-Por.



Figure S4. The Raman mapping of an oxidized silicon substrate functionalized with Co-Por.



Figure S5. The Raman mapping of an oxidized silicon substrate functionalized with Co-Phc.

II. TEM analysis.



Figure S6. TEM observations of pristine SWNTs synthesized from 0.05 nm Ru layer at 850° C under atomic hydrogen (H_{at}).



Figure S7. TEM observations of SWNTs functionalized with Co-Por. (a) SWNTs synthesis from 0.05 nm Ru layer at 850°C under H_{at} . (b) HR-STEM-BF of Co-Por. (c) STEM-HAADF image of functionalized SWNTs with Co-Por. (d) HR-STEM-HAADF image zoom of the area marked by the red dotted rectangle in (c) showing functionalized SWNTs.



Figure S8. TEM observations of SWNTs functionalized with Co-Phc. (a) HR-TEM image of functionalized SWNTs with Co- Phc. (b) HR-TEM image zoom of the area marked by the red dotted rectangle in (a) showing one functionalized SWNT.



Figure S9. STEM-HAADF-EDS line scan analysis on individual functionalized SWNTs with Fe-Por: (a) STEM-HAADF micrograph of the chosen area for the analysis. (b) EDS-STEM line scan with the Nitrogen (in blue), Iron (in red) and Ruthenium (in black) concentrations recorded along the yellow arrow in (a).



Figure S10. STEM-HAADF-EDS line scan analysis on individual functionalized SWNTs with Co-Por: (a) STEM-HAADF micrograph of the chosen area for the analysis. (b) EDS-STEM line scan with the Nitrogen (in blue), Cobalt (in green) and Ruthenium (in black) concentrations recorded along the yellow arrow in (a).



Figure S11. EDS-STEM chemical analysis on individual functionalized SWNTs with Co-Phc: (a) STEM-HAADF micrograph on the chosen area for the analysis. (b) EDS-STEM line scan with the Nitrogen (in blue), Cobalt (in green) and Ruthenium (in black) concentrations recorded along the yellow arrow in (a).



Figure S12. STEM-HAADF-EDS chemical mapping recorded on a larger area obtained by superimposing the elemental maps recorded for the carbon $K\alpha = 0.27$ eV -ionization edge (represented in red color), the silicon $K\alpha = 1.94$ eV ionization edge (represented in dark blue color), the iron $K\alpha = 6.39$ eV -ionization edge (represented in yellow color), the chlorine $K\alpha = 2.62$ eV -ionization edge (represented in orange color) and the oxygen $K\alpha = 0.52$ eV -ionization edge (represented in green color) where the nitrogen signal is slightly visible ($K\alpha = 0.392$ eV -ionization edge; blue color).

III. Theoretical calculations.

The SWNT (8,0) was modelled by a supercell of 5×5 , with 160 atoms. All optimizations and electronic properties are performed using the PBE0 functional [1] and the 6-31G** basic set [2]. The PBE0 functional has been chosen to perform this work as it has been found suitable for the description of extended systems such as SWNTs, especially the band gap [3]. The long-range van der Waals interactions were considered for all calculations by using the

Grimme's PBE0-D3 combined with Becke-Johnson damping D3(BJ) [4] which improves the description of the long-distance electronic correlations and hence, the interactions between the functionalizing molecules (phthalocyanine/porphyrin) and SWNT (8,0) surface. For the geometry optimizations and the evaluation of the Fermi energy, the 10×10 grid was applied to represent the Brillouin zone. A denser grid of 50×50 was used for the band structure.

The SCF energy convergence was achieved using LEVSHIFT 10 1 and FMIXING 30. The truncation of the coulomb and exchange were controlled by five thresholds, 11,11,11,15 and 30. (see CRYSTAL manual in Ref. [5] for exact details). In all the calculations, the SCF energy threshold value was set to 10⁻⁷ Hartree (default value), the number of alpha and beta electrons are defined by using the SPINLOCK keyword.

The geometries of the complexes were fully optimized, the binding energies (E_b in kJ/mol) and minimal distance (d_m in Å) are given in Table S1, according to the equation:

$$E_{binding}^{CP} = E_{AB}^{ab} - \left(E_A^a + E_B^b\right) - \left(E_{A^*}^{ab} + E_{B^*}^{ab}\right) + \left(E_{A^*}^a + E_{B^*}^b\right)$$
(1)

where E_{AB}^{ab} is the energy of the complex AB at its equilibrium geometry using the total complex basis set, ab; E_A^a is the energy of the isolated fragment A at its equilibrium geometry (idem for B) using the fragment basis set, a.

 $E_{A^*}^{ab}$ is the energy of the fragment *A* at the equilibrium geometry in the complex *AB* using the total complex basis set, *ab* with *B* "ghost" massless atom (idem for *B*); $E_{A^*}^a$ is the energy of the fragment *A* at the equilibrium geometry in the complex *AB* (idem for *B*) using the fragment basis set, *a*.

Table S1. The binding energies (E_b in kJ/mol) and minimal distances between Co and a C atom of the SWNT (d_m in Å) at the PBE0-D3/6-31G** levels of theory using CRYSTAL using equation (1)

System	E _b (kJ/mol)	$d_{m}(A)$
SWNT (8,0)_Co-Phc	-124.69	3.02
SWNT (8,0)_Co-Por	-125.74	3.27

Table S2. The net electron transfer (Δq) from Mulliken analysis at PBE0-D3/6-31G**levels of theory using CRYSTAL

System A_B	$\Delta q(A)$ (e)	$\Delta q(B)$ (e)	$\Delta q(A) + \Delta q(B)$
SWNT (8,0)_Co-Phc	-0,0571221	0,0571226	5E-07
SWNT (8,0)_Co-Por	-0.0495356	0.0495362	6E-07

IV. Fabrication of the FET devices.

All the electronic devices procedures were homemade and the corresponding work has been previously published [6-7].



Figure S13. I_{ds} vs V_g characteristics for CNTFET before (red curve) and after (black curve) breakdown process.



Figure S14. Scanning electron microscope (SEM) image showing a top view of an interdigited device consisting of a large number of SWNTs grown from Ru catalyst with the presence of some aggregates of Fe-Por.



Figure S15. Number of devices and corresponding $\Delta V_{th}(V)$ values.



Figure S16. I_{ds} vs V_g characteristics for a) CNTFET (black) and the same CNTFET modified with Co-Por (red). $V_{ds} = 2V$.



Figure S17. I_{ds} vs V_g characteristics for a) CNTFET (black) and the same CNTFET modified with Co-Phc (red). $V_{ds} = 2V$.

Mobility calculation:

The total capacitance, C_T , of a CNTFET based on a single SWNT is the series combination of a geometrical capacitance, C_G , and of a quantum capacitance (or density of state capacitance), C_Q , originating from the extra energy needed when adding carriers above the Fermi level of the conducting SWNT [8]. This quantum capacitance can be approximated by:

$$C_{Q} = \frac{4e^{2}}{\pi \hbar v_{F}}$$
 Eq.1

Where e is the elementary charge and v_F is the Fermi velocity of carriers ($v_F = 8x10^7$ cm/s and $C_Q \sim 4x10^{-12}$ F/cm [9]).

The geometrical capacitance corresponding to a metallic wire on a metal plane is given by:

$$C_G \approx \frac{2\pi \varepsilon_0}{Ln(4t_{OX}/d)}L$$

Eq.2

where $\varepsilon = 3.9$ for SiO₂, t_{ox} is the oxide thickness and d and L are respectively the diameter and length of the nanotube [10]. For a dielectric thickness of 100 nm and a nanotube diameter of 1.5 nm, C_G ~ 3.88×10^{-13} F/cm, *i.e.*, less than 10% of C_Q. Because the 2 capacitors are in series, it turns out that C_T ~

C_G, meaning that the effect of the quantum capacitance can be neglected. When an array of SWNTs is considered, the geometrical capacitance (per unit area) to be taken into account is more complex (ref. 4):

$$C_{GA} = \frac{2\pi\varepsilon_0\varepsilon}{\Lambda_0 Ln \left[\frac{2\Lambda_0}{\pi d} \sinh \frac{2\pi t_{ox}}{\Lambda_0}\right]}$$
Eq.3

where Λ_0 represents the average distance between SWNTs on the surface. From this expression, we can see that when the SWNT array is sparse (few SWNT/unit length), Λ_0 tends to be large and sinh $(2\pi t_{ox}/\Lambda_0) \sim 2\pi t_{ox}/\Lambda_0$. The geometrical capacitance of the array, C_{GA} , is therefore the product of the capacitance of an isolated SWNT (C_G above), multiplied by the number of tubes $(1/\Lambda_0)$.

On the other hand, when the tube density is high, $\sinh(2\pi t_{ox}/\Lambda_0) \sim (1/2)\exp(2\pi t_{ox}/\Lambda_0)$, so that C_{GA} approaches the value of a planar capacitor (per unit area)

$$C_{p} = \frac{\mathscr{E}_{0}}{t_{ox}}$$
Eq.4

Note that this approximation underestimates the carrier mobility values.

Once the coupling capacitance C determined (depending on the SWNT density), the carrier mobility (when the CNT-FET is operated in the linear region) may be evaluated as:

$$\mu = \frac{L}{WCV_D} \left(\frac{dI_D}{dV_G}\right)_{V_D}$$
Eq.5

where L and W are respectively the length and width of the transistor and V_D is the (constant) drain voltage and dI_D/dV_G is taken in the subthreshold region.

Subthreshold Region

Subthreshold swing shows how sharply the drain current drops with the gate potential, or in terms of a device performance, it means how sharply the transistor is turned off. Subthreshold swing is a reciprocal value of subthreshold slope. For a MOSFET, it can be calculated as:

$$S = (\ln 10) \frac{\partial V_g}{\partial \ln I_d} = (\ln 10) (\frac{kT}{q}) (\frac{C_{OX} + C_D + C_{it}}{C_{OX}})$$
Eq.6

where C_{OX}, C_D, and C_{it} are the oxide, the depletion layer, and the interface trap capacitance per area respectively [11]. In case of a Schottky source-drain transistor, the reader can consider the appropriate capacitances, such as a Schottky contact capacitance, etc. instead of those given in Equation 6. Subthreshold swing is usually expressed in mV/dec (decade). retical limit of S is:

$$(\ln 10)(\frac{kT}{q}) \approx 60mV/dec$$

at room temperature. Typically up-to-date MOSFETs used in processors and in memory devices have $S \approx 80 \div 100 mV/dec$.

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