Supplementary Information for

“Chemical Bonding of Partially Fluorinated Graphene”

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1. Computational method

We used the programs provided with the QUANTUM-Espresso toolkit$^1$ to carry out density functional theory (DFT) calculations. We used an energy cutoff of 100 Ry, norm-conserving pseudopotentials$^2$, and a generalized gradient approximation for the exchange and correlation energy functional$^3$. Within our semi-local DFT approach, London dispersion interactions were accounted for within the semi-empirical corrective scheme proposed by Grimme$^4$. To compute core level X-ray photoelectron spectroscopy (XPS) binding energies, we used the core-excited pseudopotential technique$^{1,5,6}$. This method allows to compute core-level binding energies taking into account for both the vertical photo-excitation transition (from the core to the vacuum level) and core-hole final-state relaxation effects. To generate norm conserving pseudopotentials for regular and photo-excited atomic relaxation species, we used the fhi98PP package$^7$.

Γ-point calculations were carried out by using the CP code of QUANTUM-Espresso$^1$. In these calculations, we used large periodic model structures of partially fluorinated graphene. The PWscf code was used to carry out periodic DFT calculations based on the use of smaller supercells and dense $k$-point meshes in the corresponding Brillouin zones. Our model structures mimicked single-layer graphene and bi-layer graphene hosting selected distributions of fluorine species. In all cases, the periodic supercells included a 12-Å vacuum region separating the modified graphene systems. Total energy and structural optimization calculations were considered converged when energy differences were less than 0.002 eV and forces were less than
0.05 eV/Å, respectively. An extensive set of calculations was carried out to verify the correctness of our calculated quantities such as formation energies and core level binding energies.

2. Bonding energies of fluorine species and graphene

To calculate formation energies, we used the following formula:

$$\Delta E = E(G + nF) - E(G) - \frac{1}{2} E(F_2) \cdot n,$$

where $E(G+nF)$ is the DFT energy of a model structure of graphene bonded to an arrangement of $n$ fluorine atoms, and $E(G)$ and $E(F_2)$ are the total energies of graphene and $F_2$, respectively. In the following figures and in the main text, we reported and discussed formation energy values given per F unit, i.e. $\Delta E/n$; henceforth this latter quantity will be simply refereed as to $E$. We point out that our DFT scheme gives the following results for the $F_2$ molecule: a bond length of 1.44 Å, a vibrational frequency of 967.3 cm$^{-1}$, and a binding energy (including zero-point correction) of 1.81 eV. These computed quantities agree well with the experimental data of 1.42 Å, 916.9 cm$^{-1}$, and 1.65 eV. Further, our calculations give an electron affinity for atomic F and a work function for single-layer graphene of 3.57 eV and 4.22 eV, respectively. These two latter quantities agree well with the experimental data of 3.41 eV$^8$ and 4.55 eV$^9$, respectively. Overall, each of the above computed physical property is within at most 10% from the respective experimental estimate. We expect the formation energies (per F unit) computed in our study to have a similar accuracy.

Figure S1 shows the formation energy of a single fluorine species in either the form of anion or the chemisorbed state in bi-layer graphene. The anionic species was held fixed at mid-way between the two graphene layers, while the chemisorbed species was considered to be exposed on either an inner or outer carbon face of the bi-layer structure (Figure S1). We considered interlayer distances between the graphene layers between 3.5 and 6 Å, and for each configuration we calculated the energy of the three fluorine species. In these calculations, the interlayer separation was constrained to remain constant. The results of these calculations are shown in Figure S1 and discussed in the main text of the article.

![Figure S1. Formation energy of an F anion (black discs) intercalated in bi-layer graphene, and of an F species chemisorbed on graphene with F at either the interior (red discs) or exterior (blue discs) of the bi-layer structure. The energy of these three fluorine species is plotted vs. the distance between the graphene layers. A schematic illustration of bi-layer graphene and the three fluorine species is shown on the right side.](image-url)
Figure S2. Ball and stick illustration, binding energy, and bond length of fluorine species chemisorbed on graphene in dimer (top), trimer (2nd row of boxes from the top), and tetramer complexes (3rd row of boxes from the top). Energy values in the boxes are calculated by referring the formation energy per F unit of the fluorinated graphene complexes to that of a single F species on graphene, shown on the top right corner. In the case of trimer and tetramer complexes, the bond length value in the boxes refers to the F-C bond circled in red. C and F atoms are colored in gray and blue, respectively.

Figures S2 and S3 shows fluorine species chemisorbed on single-layer graphene forming agglomerates of F-C bonds on graphene of various sizes and geometry: dimer, trimer, and tetramer complexes, as well as infinite ordered structures. The energy values reported in Figures S2 and S3 are given per F unit and are referred to the energy of an individual F species on graphene. The results reported Figures S1, S2, and S3 are summarized in Figure 2 of the main article and therein discussed. The main results deducible from these calculations and energy values are that F species chemisorbed on graphene attract each other, and that agglomeration favors the formation of two classes of clusters/condensates of F-C bonds. In the first type of agglomerates, the F species are chemisorbed alternatively on both sides of graphene in ortho position one another. In the second type, the F-C bonds are in para position one another and are exposed only on one side of the carbon plane.
**Figure S3.** Ball and stick illustration, binding energy, and bond length of fluorine species chemisorbed on graphene forming infinite and ordered agglomerates of F-C bonds presenting various possible geometries. Energy values are calculated by referring the formation energy per F unit of fluorinated graphene complex to that of a single F species on graphene, shown on the top right corner of Figure S2. C and F atoms are colored in gray and blue, respectively.

### 3. F1s and C1s core level XPS energy shifts

To calculate 1s core-level binding energies of F and C atoms of (model structures of) partially fluorinated graphene, we used the core-excited pseudopotential technique. The accuracy of this methodology and of the photo-excited pseudopotential for C was extensively tested in previous studies of graphene oxide. To validate the photo-excited pseudopotential for F, we considered a set of molecules containing F in various different bonding states and whose experimental XPS F1s core-level binding energies were available. Calculated and experimental core-level binding energies (referred to that of F in the F2 molecule) are compared in Figure S4. This comparison shows that computed and experimental core-level energy shifts agree well over a wide energy interval; the average absolute energy deviation between the two sets of data is 0.16 eV.
**Figure S4.** Experimental vs. calculated 1s core-level energy shifts (open circles) of F atoms in selected C-, O-, H- and F- containing molecules. Ball-and-stick illustrations or the molecules are also shown, with C, O, H, and F atoms colored in gray, red, white, and blue, respectively. All core-level energy shifts are referred to that of F in F₂.

Figures S5 through S8 (and Figures 3 and 4 of the main article) report the results of DFT calculations carried out to compute 1s core-level energy shifts of C and F species of partially fluorinated graphene. In these calculations, we considered a variety of model structures of partially fluorinated graphene, in which F was present in the isolated form, and in dimeric, trimeric, tetrameric, and/or larger complexes whose geometrical features belonged to one of the following three classes. First, F species alternating on both sides of graphene in ortho position one another; this type of bonding configuration is indicated as $(\text{FC})_n$, and it leads to highly stable as well as dense (F/C=1 in the interior of large agglomerates of this type) domains of fluorinated graphene. Second, F species chemisorbed only on one side of graphene, in para position one another; this type of bonding configuration is indicated as $(\text{FC})_n$, and it leads to stable fluorinated-graphene domains whose F/C ratio reaches a value of 0.25 in the interior of large agglomerates of this type. The third type of clusters comprises of F species chemisorbed in either ortho or meta position one another, only on one side of the graphene layer. This latter class of complexes is energetically unfavorable, and for this reason it has not been considered and discussed in the main article. The model structures representing various plausible configurations of partially fluorinated graphene were used to compute core level binding energies and investigate the nature of F-C bonds in this fluorinated graphene. To align core-level binding energies computed by using the various model structures (and DFT), we adopted the following strategy. Each model structure of partially fluorinated graphene was constructed such as to include an area (sufficiently large) of pristine graphene. The core-level binding energy computed for a C(sp²) species belonging to such region was used as zero-energy reference for the C1s core-level energy shifts. Furthermore, in the model structures we also included a single F species chemisorbed on graphene, on a region of the carbon layer sufficiently distant from any other fluorine complex (see Figures S6 and S7). The F1s core-level binding energy of this latter species was used as reference zero-energy core-level energy shifts for the fluorine species included in the model structure of fluorinated graphene. Thanks to this strategy, we were able to obtain the results shown in Figures S5, S6, and S7 as well as in Figures 3 and 4 of the main text.
Figure S5. F-C bond length (ordinates) and F1s core level energy shift (abscissas) of fluorine species chemisorbed on graphene in various bonding environments. The results reported in this complement those reported in Figure 3 of the main article. See caption of Figure 3 of the main text for conventions and further details. The color of the vertical segments and open circles is used to establish the correspondence between core level energy shift and the fluorine species drawn in the ball-and-stick illustration. The height of the vertical segments is used to show the length of the F-C bonds in the various bonding environments. The F1s core level binding energies calculated from DFT are referred to that one of F in single F-C species chemisorbed on a pristine region of graphene. The core-level energy shift of an F anion in bi-layer graphene is also reported on the right (vertical dashed segment).

<table>
<thead>
<tr>
<th>species</th>
<th>d(F-C) (Å)</th>
<th>ΔE(F1s) (eV)</th>
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<tbody>
<tr>
<td>(FC)</td>
<td>1.55 Å</td>
<td>0.7 eV</td>
</tr>
<tr>
<td>1(FC)</td>
<td>1.46 Å</td>
<td>2.0 eV</td>
</tr>
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<td>2(FC)</td>
<td>1.43 Å</td>
<td>2.8 eV</td>
</tr>
<tr>
<td>3(FC)</td>
<td>1.41 Å</td>
<td>3.5 eV</td>
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</table>

Figure S6. F1s core-level energy shifts calculated from DFT of F species in model structures of partially fluorinated graphene consisting of agglomerates of F-C bonds of various geometry. Each panel shows top and side view of the periodic model structure used in the DFT calculations, as well as a table reporting the values of the 1s core-level energy shifts of selected F species. Each model structure comprise a dense agglomerate of F-C bonds, a dimer complex, and a single F-C species on a pristine region of graphene. a), b), and c) show agglomerates of the type 2(FC) (i.e. F species alternating on both sides of graphene in ortho position one another) with F-C bonds arranged as in the “boat”, “chair”, and “zigzag” geometries, respectively. In panel d), the cluster is of type 1(FC), i.e. with F-C bonds on one side of graphene in para position one another.
F1s core-level energy shifts computed from DFT are excellent indicators of both the chemical bond and local environment of the F species in partially fluorinated graphene. In particular, our results (summarized in the main text and reported in Figures S5, S6, S7, and S8, and in Figures 3 and 4 of the main article) show that:

1) F-C bonds in the form of isolated (FC)$_1$ species have a semi-ionic nature. They exhibit a character (they give rise to a F1s core-level energy shift) mid-way between that of F forming a covalent bond at graphene edges and that of F anions intercalated in multilayer graphene.

2) F-C bonds belonging to the interior of agglomerates of type $(2)(FC)_n$ exhibit a covalent nature, similar to that one of F species saturating bonds at graphene edges.

3) F-C bonds belonging to the interior of agglomerates of type $(1)(FC)_n$ exhibit a character intermediate between the semi-ionic and covalent bonds of the two species above.

4) F species at the periphery of $(1)(FC)_n$ aggregates, or belonging to small clusters of the same type, form F-C bonds possessing an ionic character stronger than that of F-C bonds in the interior of large $(1)(FC)_n$ aggregates, but not as strong as they were completely isolated on a pristine region of the graphene layer.

5) F species at the periphery of $(2)(FC)_n$ aggregates, or belonging to small clusters of the same type, form F-C bonds possessing a covalent character weaker than that of F-C bonds in the interior of large $(2)(FC)_n$ aggregates, but not as weak as they belonged to large $(1)(FC)_n$ aggregates.

6) F-C bonds in agglomerates consisting of F-C bonds on one side of the graphene layer in meta position one another possess a strong semi-ionic nature.

7) F1s core-level binding energy values and F-C bond lengths show a marked level of correlation, further corroborating the fact that all the above F species form different types of bonds with graphene.

<table>
<thead>
<tr>
<th>species</th>
<th>d(F-C) (Å)</th>
<th>ΔE(F1s) (eV)</th>
<th>ΔE(C1s) (eV)</th>
</tr>
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<tr>
<td>C(sp$^3$) (x)</td>
<td>--</td>
<td>--</td>
<td>0</td>
</tr>
<tr>
<td>C(sp$^2$)-(FC)$_x$ (•)</td>
<td>--</td>
<td>--</td>
<td>-0.5 eV</td>
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<tr>
<td>(FC)$_1$ (o)</td>
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<td>1.8 eV</td>
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Figure S7. 1s core-level binding energies of F and C species at zigzag- and armchair-type graphene edges. To align the core-level binding energies of these species to that of F or C species on or in the carbon basal plane, the model structures of the graphene edges include a single F species and a F-C dimer in the central region of the nano-ribbons. The tables report the core-level energy shifts obtained from DFT; see captions of previous figures for color and stylistic conventions.
**Figure S8.** F-C bond length vs. F1s core-level energy shift of F species chemisorbed on graphene in various bonding states, as obtained from our DFT calculations. The color of the symbols refer to F species belonging to the categories shown in Figures S5, S6, and S7, i.e. from left to right, F species at graphene edges (orange), F in the interior of \( 2\text{(FC)}_n \)-type domains (cyan), F at the periphery of the latter type of fluorinated-graphene domains (light blue and purple), F in the interior of \( 1\text{(FC)}_n \)-type domains (purple), F at the periphery of this last type of fluorinated-graphene domains (pink and magenta), F in the interior of domains with F species chemisorbed on the same side of graphene in meta position one another (magenta), at the periphery of this type of energetically unfavorable fluorographene domains (dark green and light green), and finally isolated F species on the graphene layer (light green). The F species above, in the same order, form bonds with graphene showing increasing F-C bond lengths and ionic character.

**References**


