Highly Fluorinated Graphene

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We give the results of density functional calculations for graphene with a widely varying fluorine adsorptions. We give a systematic analysis of the adsorption energies, lattice constants, bulk modulus, bandgap openings, and magnetic properties. We find that a number of different adsorption geometries and a range of physical properties can occur for each adsorbate coverage. The systems are found to range from metallic to semiconducting with widely vary band gaps, and a number of interesting magnetic phases are found. We expect that many of these structures may occur in real materials systems. Further that a listing of the properties found here may help in determining what fluorinated graphenes are produced experimentally.

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I. INTRODUCTION

Since its experimental realization graphene has been under intense study because of its exceptional physical properties including its high electrical conductivity, strength, and elasticity. However, graphene is relatively inert chemically and is a zero band gap semiconductor; thus many of its properties need to be modified for use in applications.

Methods to modify the electronic and mechanical properties of graphene include substrate interactions, electric and magnetic fields, strain, and chemical functionalization. Surface chemical functionalization is particularly attractive because graphene consists of only surface atoms. A number of adsorbates have been studied, including H, F, O, and NH$_2$. This work will focus on chemical functionalization with fluorine.

The fluorination of carbon-based systems has attracted considerable attention. Much work has been directed at the fluorination of graphite, particularly in connection with lubrication. Considerable experimental and theoretical work has been done on fluorination of buckyballs and carbon nanotubes. Fluorine adsorption is a simple chemical functionalization that increases the reactivity of sp$^2$ bonded graphene and opens a wide range of modifications. In addition it enables tuning of band gaps and doping for use in electronics. Experiments have shown dramatic changes in the electronic and structural properties of graphene by increasing the degree of fluorination. Theoretical work on fluorinated graphene has focused mainly on fully covered systems and on systems with low fluorine coverage, with only a few studies that considered several high coverage fluorinated graphene systems.

In this work we consider varying degrees of fluorination (stoichiometries) on graphene surfaces and a number of different arrangements of F atoms (motifs) of the F on surface for each stoichiometry. The overall stoichiometry of F on a fluorinated graphene surface is denoted by C$_m$F$_n$ where there are n F atoms adsorbed onto m C atoms. In Section II we discuss the computational methods used here. In Section III the mechanical, electrical, elastic, and magnetic properties of fluorinated graphene of varying stoichiometries and motifs are presented. A listing of the stoichiometries and motifs studied here and their calculated properties is given in Table I. We will make frequent reference to this table. Concluding remarks are found in Section IV.

II. COMPUTATIONAL METHODS

We used the ab initio plane wave code PWscf, which is part of Quantum Espresso, to study supercells of fluorinated graphene with periodic boundary conditions. The generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) was used to account for exchange-correlation effects. Vanderbilt ultra-soft psuedopotentials with wave function energy cutoff of 30 Ry was employed. We found that an 8-by-8 Monkhorst-Pack mesh sampling of the Brillouin zone was sufficiently dense for the total energy to be converged. To speed up the SCF conversion during the
| Item | Stoichiometry | %F | C | A | Gap (eV) | F/A | Charge (eV) | C/A | Pol. Enthalpy (eV) | C/A |
|------|--------------|----|---|---|---------|-----|------------|-----|-------------------|-----|
| 1    | 0.11         | 0.2 | 1 | 2 | 1.528   | 0.06 | -0.28      | 0.13 | 0.004            | 0.00 |
| 2    | 1.2          | 0.7 | 2 | 3 | 2.245   | 0.24 | 0.028      | 0.17 | 0.004            | 0.00 |
| 3    | 0.2          | 1.6 | 6 | 2 | 3.043   | 0.34 | 0.028      | 0.17 | 0.004            | 0.00 |
| 4    | 0.11         | 1.2 | 2 | 1 | 2.875   | 0.29 | 0.028      | 0.17 | 0.004            | 0.00 |
| 5    | 1.2          | 0.7 | 2 | 3 | 2.245   | 0.24 | 0.028      | 0.17 | 0.004            | 0.00 |
| 6    | 0.2          | 1.6 | 6 | 2 | 3.043   | 0.34 | 0.028      | 0.17 | 0.004            | 0.00 |
| 7    | 0.11         | 1.2 | 2 | 1 | 2.875   | 0.29 | 0.028      | 0.17 | 0.004            | 0.00 |
| 8    | 1.2          | 0.7 | 2 | 3 | 2.245   | 0.24 | 0.028      | 0.17 | 0.004            | 0.00 |
| 9    | 0.2          | 1.6 | 6 | 2 | 3.043   | 0.34 | 0.028      | 0.17 | 0.004            | 0.00 |

TABLE 1: listing of the molecular and physical properties for all of the PAMAM structures studied. Throughout the paper we will refer to a particular structure by its number given in the first column. In order from left to right, the columns contain: the item number, stoichiometry, atomic percentage of fluorine. Atomic percentage of fluorine, listing of C atoms, listing of F atoms, total ionization energy of the molecule, the charge transfer per F atom, band gap, ground state polarization, saturation moment, net polarization, and the net chirality energy.
FIG. 1: Placement of carbon atoms in a two-by-two unit cell of graphene. The numbers are used to denote the carbon atoms in the unit cell that have fluorine atoms attached to them. The dark (light) gray spheres represent the atoms in the A (B) graphene sublattice. In the one-sided systems, the attached atoms would be directly over the carbon atoms coming out of the page.

structural relaxations the wave functions and potentials were extrapolated to second order from the preceding ionic steps.

In this work we studied a large number of periodic fluorinated graphene systems using a 2-by-2 graphene cell as the basic unit. This size of supercell is important because as Li et al. have shown, the longest F-F distance that can produce a magnetic ground state is about 4.92 Å, which corresponds roughly to a 2-by-2 supercell. We will refer to the structures studied here by the Item numbers in the first column of Table I. The second and third columns of Table I give the stoichiometry and atomic % F of each system. Figure 1 labels the positions of the C atoms in the unit cell. The starting configuration of each system had F atoms directly above, or below, the C atoms. The motifs of the F atoms in each system are given in the columns labeled “Above” and “Below” in Table I where the numbers correspond to the C atom having a F adatom attached above or below the graphene plane. The calculated values of the lattice parameters were obtained by computing the total energy of the F-graphene system at a set of lattice constants and then fitting the resulting curve with the Birch-Murnaghan equation of state. An inter-layer spacing (c lattice parameter) of 24.6 Å was used in the direction perpendicular to the graphene plane.

When giving band structures and electronic properties we have taken into account the possibility of ferromagnetic and antiferromagnetic spin orderings. When computing the ferromagnetic case, each F atom had an initial spins excess of 0.99 μB. In the antiferromagnetic case each of the F atoms adsorbed onto the graphene A sublattice had a spin excess of 0.99 μB and the F atoms adsorbed onto the graphene B had the opposite spin. The ordering with the lowest total energy is the ground state. The adsorption energies, band gaps, intrinsic spin polarizations, and charge transfers in Table I and in the figures are the values found in the ground state configuration.

III. RESULTS AND DISCUSSION

The calculated band structures of all CxF phases studied here can be described by reduced sets of maximally localized Wannier functions, MLWF. These are localized, tight-binding-like Wannier orbitals obtained by band interpolation, which are useful for electronic transport and elasticity models. They describe the occupied bands and are a good approximation to the lowest conduction bands. Wannier90 was used to produce MLWF from the Block-like wavefunctions used in Quantum Espresso. In performing the Wannierization, we specified the k-point positions of a 4x4 two-dimensional Monkhorst-Pack mesh sampling of the Brillouin zone, which was shifted to include the Γ-point. With these we can reproduce the valence band of CxF and the lowest branches in the conduction band.

The adsorption energy per F atom versus atomic % F given in Fig. 2 (A) and in Table II column 6 may be used in understanding the experimental coverage of graphene by F. The adsorption energy per F, E_A was computed using

$$E_A = (E_{GR,nF} - (E_{GR} + n_F E_F))/n_F$$  \hspace{1cm} (1)$$

where $E_{GR,nF}$ is the ground state total energy of the fluorinated graphene, $E_{GR}$ is the ground state total energy of graphene, $E_F$ is the energy of a single F atom, and $n_F$ is the number of F atoms in the system. Using this definition of the adsorption energy per F atom the structures with larger adsorption energies have lower ground state total energies. We find that the one-sided coverage with the maximum adsorption energy is at 0.2 atomic % F. The dotted line in Fig. 2 (A) is used to show the pattern of the maximum adsorption energy for 1-sided motifs. We also see that the maximum adsorption energies of the two-sided stoichiometries increase (solid line in Fig. 2(A)) until full coverage (0.5 atomic % F). These two features are consistent with experiment.
highest per F adsorption energy has F atoms at the para position sites (Table I Item 4)\cite{42}, while the fully fluorinated system with the highest adsorption energy is in the chair configuration (Table I Item 91)\cite{23,29}. Using modeling of the C Kα spectroscopy Bulusheva et al. suggested that C2F is in a configuration similar to Item 26, which we find to be one of the most energetically favorable C2F motif\cite{12}. Finally, we note that the adsorption energy per F atom vs atomic % F is a convenient way of graphically representing other data. We will use it in Figs. 5 and 6 to relate conduction and intrinsic polarization properties to the fluorine coverages and adsorption energies.

We note several points about the calculated absorption energies. For stoichiometries that have both one-sided and two-sided motifs, the motif that is the highest adsorption energy is always two-sided. The one sided (Item 4) and two sided (Item 5) C2F coverages with the F in the para positions (adatoms on the C atoms labeled 1 and 6 in Fig. 1) are similar in energy, but when the F atoms are in the ortho (adatoms at 1 and 2) or meta (adatoms at 1 and 7) positions the energy difference is large\cite{12}. This is likely due to the interactions between the F atoms in the ortho and para cases and the relatively smaller interaction in the para configuration. It also appears that the coverages that have an even number of F atoms in the 2x2 supercell have higher maximum adsorption energy than their surrounding odd coverages. Sublattice imbalance is defined as the absolute difference between the number of F atoms on the A sublattice and the B sublattice. In the cases where a particular stoichiometry allows for different values of sublattice imbalance the motifs that minimize the imbalance have a lower total energy\cite{3}.

The optimal lattice constant, as found by the Birch-Murnaghan equation of state, of each motif is given in Table I column 7 and Figure 2 (B). It shows that the lattice constant tends to increase as the fluorination increases. For graphene we found an equilibrium lattice constant of 2.4607 Å in good agreement with the experimental value of 2.4602 Å\cite{23}. For CF, in the chair configuration, we found a lattice constant of 2.61 Å which is near the value calculated by others\cite{47,48,49}, but is much larger than the experimental value obtained by Nair et al., 2.48 Å\cite{10}. Artyukhov and Chernozatonskii claim that this difference can be explained if the surface has a structure like Item 3\cite{48,50}. Alternatively, this could result from domains of CF of one motif, or different motifs, where the average lattice constant could be in the range found experimentally. That domains of different CF motifs could exist is supported by the finding of Charlier et al. that a diffusion barrier of about 2.7 eV exists between the chair and boat configurations (Items 51 and 52), effectively blocking on CF motif from turning into another CF motif\cite{51}. Our results also agree remarkably well with the C2F lattice constant values reported in Ref. 27.

We also performed variable cell optimizations on a representative subset of motifs (the set of motifs with the highest adsorption energy per F atom for each stoichiometry) to determine if the fluorination of graphene caused significant changes in the Bravais lattice\cite{50}. These calculations allow the lattice parameters to be optimized as well as the positions of the atoms within the cell. The results gave lattice constants that were approximately equal (to within a few hundredths of an Angstrom) to the values given in Table I and lattice angles that were consistent with a hexagonal lattice. Thus, a simple two-dimensional hexagonal lattice is sufficient for describing fluorinated graphene\cite{10}.

When fitting the total energy versus crystal volume curve with the Birch-Murnaghan equation of state one of the parameters that can be extracted is the bulk modulus. With fluorinated graphene there is no well defined way to account for its thickness. Thus, we cannot accurately compute the bulk modulus. Therefore, Figure 2 (C) and Table I give the one-dimensional correlation to the bulk modulus as a way to qualitatively discuss the change in the elasticity with fluorination. These values were computed by fitting lattice constants versus total energies with the Birch-Murnaghan equation of state. Pristine graphene has an elastic modulus of 17.2 eV/Å. The values computed for fluorinated graphene tend to decrease as fluorination increases. Sahin et al. argue that the rehybridization of the carbon atoms into sp\(^3\) structures is the main cause of the change in elasticity\cite{23}.

In Table I column 9 we list the average C-F bond lengths for each motif (shown in Fig. 2 (D)). Although the theoretical lattice constants given in the literature for armchair CF (Item 51) are all similar, there is a wide range of reported theoretical C-F bond lengths\cite{21,20,28,33}. Our results are near the lower end of the theoretical values reported. Our results are in the middle of the range of reported C-F bond lengths for systems like C2F and C4F. Experimental values for these two systems fall over a wide range of values, from 1.36 Å to 1.64 Å, placing our results within the experimental range\cite{15,13,29}. Covalent (ionic) C-F bonds typically have bond lengths of about 1.32 Å (2.01 Å). The values that we obtain for the fluorinated graphene systems, \(d_{C-F} = [1.377, 1.554]\), indicate that the C-F bond is semi-ionic\cite{52} at low coverage and becomes more covalent as the fluorination increases. This agrees with X-ray photoemission spectroscopy which shows that the bonds are semi-ionic at coverages less then C2F, but that they become covalent at higher coverages\cite{21,29}.

To understand further the nature of the C-F bonds we computed the Löwdin charge transferred from the carbon atoms to the F atoms. Table II gives the charge transfer per F atom. The charge transfer per F atom versus average C-F bond length is given in Fig. 3. There is a general trend of more charge being pulled out of the graphene backbone as the adatom bond length increases. We suggest that the increasing charge transfer with increasing bond length results from more charge being pulled out of the carbon in order to satisfy the increasing ionic nature of the C-F bonds.

Projecting the DFT results for electronic properties onto tight-binding bands can give physical insight into binding
FIG. 2: Calculated values as a function of Fluorine coverage. The gray circles (triangles) represent structures with one-sided (two-sided) fluorination. The blue circles (red triangles) are the one-sided (two-sided) motifs that have the highest F adsorption energies at a given atomic % F. The values shown are (A) the adsorption energy per F atom, (B) equilibrium lattice constant, (C) one-dimensional analog of the bulk modulus (elastic modulus), (D) C-F bond length. The dotted (solid) black line in (A) is used to guide the eye in determining the motif of the one-sided (two-sided) structures with the highest adsorption energy per F atom. The dashed, horizontal lines in (B), (C), and (D) represent the values computed for pristine graphene. The dotted line in (D) is the length of a C-F covalent bond.

and electrical properties. We do this projection onto a set of maximally localized Wannier functions (MLWF). Figure[1] gives the DFT band dispersion plots along with the corresponding MLWF orbital projections of graphene and of several illustrative fluorinated graphene systems. In the Wannierization of the DFT results the high symmetry energy bands are disentangled separately in the following energy windows: the valence band, the localized states in the band gap, and the lowest energies of the conduction band. In the valence band, there are branches coming from s-like states centered on F atoms that are separated at very low energies (< 10 eV). The other bands are disentangled in terms of the following orbitals (Wannier states): one s-like orbital centered on each C-C pair (σ bond) including both sp² (non-fluorinated) and sp³ (fluorinated) carbons, which produce deep energy states; one s-like orbital centered on each C-F pair, also with a low energy in the valence band; one p_z-like orbital for each pair of neighboring non-fluorinated neighboring C atoms (π bond) at the top of the valence band; two p_x, p_y orbitals on each F atom accounting for the paired electrons in the p-shells of the F atoms and giving localized (non-dispersive) low energy states. For the conduction bands we interpolate only the branches in a small low-energy window that are relevant for transport models. Higher states cannot be disentangled with tight-binding orbitals because they hybridize at high energies with
an unlimited number of quasi-free surface states. We find that the lowest conduction branches are given by \( p_z \)-like orbitals centered on C-F pairs (antibonding \( \sigma^* \) states) and by a combination of \( d_{xz} \) and \( d_{yz} \)-like orbitals centered on unfluorinated C-C pairs (antibonding \( \pi^* \) states). For fully fluorinated graphene we have only the former set of orbitals.

Figures 4 (A) shows the band dispersion of graphene. The HOMO and LUMO states of graphene are composed entirely of the \( \pi \) and \( \pi^* \) molecular orbitals made from \( C_p \). Lower energy valence branches are composed entirely of \( sp^2 \) molecular orbitals. Due to the symmetry of pristine graphene, there is no hybridization between its \( \pi \) and \( sp^2 \) orbitals; therefore its energy bands are not entangled and can be interpolated in a single energy window that includes the lowest conduction bands. There are also three high-energy conduction branches created by anti-bonding \( C sp^2 \) orbitals and a set of quasi-parabolic branches from states outside the graphitic plane.

Bonds formed between the F \( p_z \) and the C \( p_z \) orbitals force the C atoms into \( sp^3 \) hybridization, breaking the symmetry of graphene. In many cases this opens a gap via the formation of new C-F bonding states deep in the valence band and C-F antibonding states in the conduction band\(^{28} \) as can be seen in Figs. 4 (B,D,E, and F). The resulting bands are entangled due to orbital hybridization, manifested as anticrossings between branches in the Brillouin zone. As the degree of fluorination is increased, the number of C-C \( \pi \) states at the top of the valence band is decreased and the number of deep C-F \( \sigma \) bonds is increased, until all \( \pi \) bonds are are removed for CF and the top of the valence band is given by \( \sigma \) bonds.

The C\(_4\)F structure (Item 4) in Fig. 4 (C) is an exception to this trend. The HOMO and LUMO states can be completely described by the hybridization of the \( C_{p_z} \) of the carbon atoms that are not bound to F atoms and the \( sp^2 \) bonding between carbon atoms, though the latter orbitals are only weakly hybridized. The difference in electronic structures between the C\(_4\)F structure discussed here and the other fluorinated graphene structures in this paper occurs because the arrangement of F atoms allows for both an aromatic ring and equal numbers of adsorbates on the graphitic sublattices.

For an odd number of non-fluorinated carbons in the supercell the result is a spin-polarized band structure. These bands are interpolated by \( p_z \)-like Wannier states centered on the unfluorinated C atoms. For example, the C\(_8\)F phase has an unpaired \( p_z \) orbital surrounded by three pairs of \( \pi \) bonds that give the valence band in Fig. 4 (B), and the C\(_8\)F\(_7\) has an unpaired \( p_z \) orbital surrounded by \( sp^3 \) carbons as in Fig. 4 (E).

Table 1 column 11 lists the band gaps of the systems. The letter C is listed instead of a numerical value in cases where the system’s Fermi level is within a band. Figure 4 (B) shows such a case. Many of the systems have indirect band gaps. The systems with indirect gaps will be less photoactive than the systems with direct gaps.

We find that the majority of the configurations studied here are semiconductors. Figure 5 (A) shows how the metallic and semiconducting configurations are distributed as functions of the adsorption energy and the % atomic F. The semiconducting systems tend to have larger adsorption energies per F, meaning that it may be hard to produce a highly fluorinated system that is metallic. We found that a filled valence band occurred only when the carbon atoms without an attached F were found in pairs or rings. Figure 5 (B) shows the distribution of band gaps versus atomic % F. We see that it is possible to tune the band gap over a wide range by F adsorption.

Trends in magnetic properties of fluorinated graphene can be understood in terms of the bipartite lattice of graphene and Hund’s rule. Each carbon atom in graphene forms three covalent bonds (\( \sigma \) molecular orbitals) leaving one electron to be part of the \( \pi \) bonding. If one C atom has a spin up electron in it’s \( p_z \)-orbital then it’s neighbors will have spin down electrons in their \( p_z \)-orbitals. The formation of the \( \pi \) conjugation effectively makes the spin polarization of...
FIG. 4: Band dispersions of: [A] graphene, [B] C4F (Table 2 Item 1), [C] C4F (Item 4), [D] C4F3 (Item 36), [E] C4F7 (Item 44), [F] CF (Item 52). The DFT results are given by light gray, dark gray, and black lines; the black lines represent the spin-up results, dark gray the spin-down results, and light gray spin degenerate results. The maximally localized Wannier function interpolation is illustrated using blue to represent the C۶p۶ bonds, red the non-bonded C۶p۶, dark green the symmetric bonds between C۶p۶ and F۶p۶, green the antisymmetric bonds between C۶p۶ and F۶p۶, and orange the F۶p۶ bonds. For clarity, [A] and [F] are for 1-by-1 supercells giving fewer bands than the other figures.

FIG. 5: (A) Plot of semiconducting and p-type doped conducting systems. The blue points are for semiconductors and the red points are for structures where the Fermi level has band crossings. (B) Distribution of band gaps versus atomic percentage fluorination. The blue circles (red triangles) are the one-sided (two-sided) motifs that have the highest adsorption energy per F atom.

the graphene sheet zero. Each neutrally charged F atom will have a spin ±1/2 excess before adsorption on to the surface. To satisfy Hund’s rule a fluorine’s p۶ electron will have to collapse into a spin state opposite to that of the C atom on which it adsorbs. As the F adsorbs onto a C atom it forms a semi-ionic bond, the covalent portion of which kills the majority of the spin polarization in the F atom while only slightly changing the spin polarization of the C atom. The formation of the C-F bond breaks the π-conjugate bonding of the C atom with its neighbors. The nearest neighbors, being the atoms which are most disturbed by the disrupted π conjugation, share the majority of the spin excess. The bipartite nature of the surface ensures that the induced spin polarization of the nearest neighbors is
shared with the other C atoms that make up the same sublattice. Further F adsorptions, depending on placement, produce strong or weaker induced polarizations in individual atoms.

Figure (A) shows the distribution of ferromagnetic and antiferromagnetic ground states versus F coverage, and (B) shows the distribution of motifs that have non-zero net spin polarizations. We find that many of the structures that are supposedly in an antiferromagnetic state in fact have a non-zero net spin polarization. Analysis of the intrinsic spin of each atom within the different motifs shows a range of magnetic orderings, including nonmagnetic, ferrimagnetic, frustrated, and antiferromagnetic. The range of orderings are due to the superpositioning of polarizations discussed in the previous paragraph. Items 17, 19, and 20 are an interesting case study: All have four F atoms bonded to C atoms 1, 3, 5, and 7, all of the F atoms are on the same side of the sheet in Item 17, while Items 19 and 20 have F atoms on both sides. In both Items 17 and 20 the ferromagnetic ordering is the ground state, while Item 17 has a strong net intrinsic polarization Item 20 has an almost zero net polarization. Item 19 has three F atoms on one side of the sheet and one F atom on the other side. In this case the antiferromagnetic order is the ground state with an intrinsic polarization of nearly 1 Bohr magnetron per unit cell, which acts like a ferromagnetic ordering. Thus, magnetic ordering is highly dependent on the motif formed by the F atoms.

Figures (C) and (E) show the net spin polarization versus the atomic percent fluorine and the imbalance of F adsorbed on each sublattice, respectively. Zhou et al. have calculated the properties of C$_4$H, C$_2$H, and CH, and they speculate that, “only half hydrogenation can introduce magnetization.” This is not the case for fluorinated graphene. We find that there is at least one motif for every stoichiometry other than fully fluorinated graphene that has a nonzero intrinsic spin polarization. Also, contrary to what may be assumed from the simplified explanation of intrinsic polarization discussed above, very few of the structures have a net spin polarization that approximately an integer multiple of one Bohr magnetron. Although we note that a couple of the C$_2$F motifs are nearly 4 $\mu_B$.

In order to estimate the thermal stability of the spin polarized states we estimated the polarization energy, $E_P$, of the fluorinated graphene systems (Figure (D) and Table I column 16). The value of $E_P$ is estimated by $E_P = E_{sr} - E_{su}$, where $E_{sr}$ is the energy of the system when computed in a spin restricted calculation, and $E_{su}$ is the energy of the system when in the ferromagnetic state (or antiferromagnetic state, whichever is energetically favorable). As is shown in the last column of Table I many of the systems have $E_P$ values that are greater than 0.03 eV making it possible for them to be stable at room temperature.

IV. SUMMARY

We have studied graphene systems for a wide range of fluorinations within density functional theory. Several atomic arrangements are possible for most stoichiometries. A wide range of structural, electronic, elastic, and magnetic properties have been calculated for them. Systems vary from metallic to semiconducting with widely varying band gaps. Electronic properties and lattice constants vary with coverage, and a rich range of antiferromagnetic and ferromagnetic phases are found. It is reasonable to expect that a variety of these phases may occur in real materials systems.

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FIG. 6: Magnetic Properties: (A) Motifs with ferromagnetic (red) and antiferromagnetic (blue) ground states. (B) Motifs with net spin polarization equal to zero (red) and non-zero (blue) net spin polarization motifs. (C-E) The gray circles (triangles) represent structures with one-sided (two-sided) fluorination. The blue circles (red triangles) are the one-sided (two-sided) motifs that have the highest F adsorption energies. (C) Net spin polarization versus fluorine coverage. (D) Polarization energy versus fluorine coverage. (E) Spin-polarization versus the difference in F adsorbed on each sublattice (sublattice imbalance).
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A quick example might best explain this. Items 4 and 7 both have two F adatoms within the supercell. Item 4 as F atoms

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bonded to C atoms 1 and 6 where both are on the same side of the graphene sheet. In Item 7 the F are bonded to the same atoms, but with one F above the graphene sheet (sticking out of the page in Fig. 1) and the other is below the graphene sheet (pointing into the page).

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37. In a few cases (i.e. Item 16) all of the F atoms are attached to the same sublattice, and thus our scheme could not produce an antiferromagnetic ordering. In these cases we ended up alternating the initial spin surplus on the F atoms. Further, in one case, Item 1, we alternated the initial spin surplus on the C atoms in order to achieve a possible antiferromagnetic structure.

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42. As a further check on this statement we also computed the absorption energies of two F atoms in meta, ortho, and para configurations in the middle of a much larger supercell that was fully relaxed, but otherwise free of defects. The systems consisted of rectangular graphene supercells that were 29.58 Å along the x-direction and 25.6176 Å along the y-direction, where the x-direction was along a zig-zag pattern of the graphene sheet. The absorption energy per F atom of the meta, ortho, and para conformations were 2.679 eV, 2.420 eV, and 2.826 eV, respectively.

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