

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263938847>

# Chemical Reactivity of Electron-Doped and Hole-Doped Graphene

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · FEBRUARY 2013

Impact Factor: 4.77 · DOI: 10.1021/jp306544m

---

CITATIONS

14

---

READS

42

## 1 AUTHOR:



[Pablo A. Denis](#)

University of the Republic, Uruguay

**104** PUBLICATIONS **1,561** CITATIONS

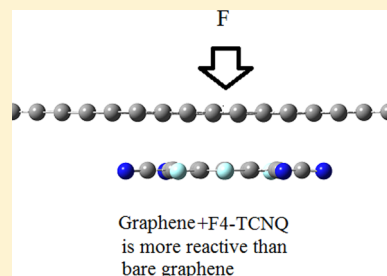
SEE PROFILE

# Chemical Reactivity of Electron-Doped and Hole-Doped Graphene

Pablo A. Denis\*

Computational Nanotechnology, DETEMA, Facultad de Química, UDELAR, CC 1157, 11800 Montevideo, Uruguay

**ABSTRACT:** The chemical reactivity of electron-doped and hole-doped graphene was studied by means of first principles calculations, on the basis of dispersion corrected density functional theory. To model hole-doped graphene, the widely known electron acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) was utilized, while the electron donor tetrathiafulvalene (TTF) was selected for the electron-doped case. The results demonstrate that the reactivity of graphene can be modified by the adsorption of electron donating/withdrawing molecules. The reactions considered were the addition of fluorine atoms and hydroxyl radicals. In both cases, it was observed that the adsorption of F4-TCNQ and TTF increased the reactivity of graphene. This outcome was expected for electron-doped graphene because we have recently shown that lithium increases the reactivity of graphene. Yet, for F4-TCNQ, the finding is surprising given that this molecule accepts 0.4  $e^-$  from graphene. The gas phase free energies of association are calculated to be negative for F4-TCNQ and TTF, but for the latter is only  $-2.5$  kcal/mol. The results obtained employing infinite models and using the VDW-DF and M06-L functionals are supported by cluster model calculations performed with the M06-2X method. When TTF was adsorbed onto graphene, a charge transfer from TTF to graphene was not observed. However, when TTF and F4-TCNQ are simultaneously adsorbed on opposite sides of the graphene sheet, the amount of charge accepted by F4-TCNQ and donated by TTF is increased. This work clearly suggests that dual doping is a useful tool to expand, even to a greater extent, the possibilities to tune the properties of graphene. Further work must be devoted to synthesize better electron donors and acceptors and thus allow for larger charge transfer.



## 1. INTRODUCTION

As early as 2007 Chen et al.<sup>1</sup> showed that 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) can induce p-type doping of epitaxial graphene grown over 6H-SiC(0001). This work opened new avenues leading to electron-doped or hole-doped graphene.<sup>2–16</sup> For example, Subrahmanyam et al.<sup>2</sup> studied the interaction of electron donor tetrathiafulvalene (TTF) and the electron acceptor tetracyanoethylene (TCNE) with few-layer graphene. These authors demonstrated that the charge transfer interaction strongly depended on the surface area. It was higher for epitaxial graphene and smaller for graphene obtained by arc evaporation of graphite in a hydrogen atmosphere. In the same vein, Varghese et al.<sup>3</sup> reported that the interaction with electron acceptor molecules (TCNE, TCNQ, TNF) is stronger than those corresponding to TTF<sup>6</sup> and DMPD, which are electron donors and induce n-type doping. Perylene-3,4,9,10-tetracarboxylic 3,4,9,10-dianhydride (PTCDA) is another electron donor molecule which has received considerable attention. Experimental and theoretical work revealed that it can be strongly stacked above graphene, induce n-type doping, and open a 0.1 eV band gap in the electronic structure of graphene.<sup>7,8</sup> When dual molecular doping is accomplished, that is combining p-type doping above and n-type doping below graphene, a band gap can be more easily opened.<sup>9</sup> Theoretical calculations have been employed to shed light into the interaction of powerful electron acceptors F4-TCNQ and TCNE with graphene. According to these first principles results, F4-TCNQ and TCNE can accept 0.3<sup>10,11</sup> and 0.44<sup>12</sup> electrons per molecule, respectively. Regarding the interaction energy, Pinto et al.<sup>10</sup>

reported that the adsorption energy of F4-TCNQ onto graphene is 27.7 kcal/mol at the LDA level, whereas Manna and Pati<sup>11</sup> determined that the adsorption energies of TCNE, TCNQ, and TTF onto graphene are 32.5, 47.3, and 31.8 kcal/mol, respectively, at the PBE/DZP level of theory. The interaction between graphene and TCNE can be improved by doping with N or B.<sup>12</sup> The adsorption of these molecules opens a small band gap, and thus, they can help tune the band gap and carrier type of graphene.<sup>11</sup> On the other hand, Zhang et al.<sup>13</sup> showed that TTF and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) transform zero gap graphene into metallic graphene, even though the modifications in the electronic structure are not enough for sensing applications. In the case of bilayer graphene,<sup>14</sup> the gap induced by TCNE is 0.3 eV, and it can be tuned by controlling the TCNE coverage.

Almost every work dealing with the interaction between graphene and organic molecules focuses on the modification of the electronic properties of graphene by molecular adsorption of the aforementioned electron donor or acceptor molecules. Nevertheless, it has been forgotten that, as ripples, the addition/removal of electrons from graphene modifies its chemical reactivity. In effect, there is experimental<sup>17</sup> and theoretical<sup>18–21</sup> evidence which indicates that electron puddles increase the reactivity of graphene. On the experimental side, Fan et al.<sup>17</sup> revealed that ionized impurities ( $Na^+$ ) in the  $SiO_2$  support layer increase the reactivity of graphene toward

Received: July 2, 2012

Revised: January 14, 2013

Published: January 23, 2013

Table 1. Graphene–F4-TCNQ and Graphene–TTF Adsorption Energies (kcal/mol) Determined at Different Levels of Theory

	model	F4-TCNQ	TTF	F4-TCNQ-TTF
M06-L/6-31G*	$\infty$ graphene $6 \times 6$	30.9	15.9	47.1 (+0.3) <sup>b</sup>
M06-L/6-311G*	$\infty$ graphene $6 \times 6$	36.0	20.1	57.2 (+1.1) <sup>b</sup>
VDW-DF/DZP	$\infty$ graphene $6 \times 6$	29.4	15.5	49.3 (4.4)
LDA/DZP	$\infty$ graphene $6 \times 6$	21.1	6.8	
M06-2X/6-31G*	C <sub>48</sub> H <sub>18</sub> nanographene cluster	30.4 (−14.5) <sup>a</sup>	15.1 (−2.5) <sup>a</sup>	45.6 (+0.1) <sup>b</sup>
M06-2X/6-311G*	C <sub>48</sub> H <sub>18</sub> nanographene cluster	35.4	19.8	55.2 (+0.03) <sup>b</sup>
M06-2X/cc-pVTZ	C <sub>48</sub> H <sub>18</sub> nanographene cluster	28.4	14.7	43.7 (+0.6)
M06-2X/cc-pVQZ	C <sub>48</sub> H <sub>18</sub> nanographene cluster	25.7	14.2	41.7 (+1.8)
M06-L/6-31G*	C <sub>48</sub> H <sub>18</sub> nanographene cluster	32.9	14.3	

<sup>a</sup>Values in parentheses correspond to free energy changes at 298 K. <sup>b</sup>Values in parentheses correspond to the difference with respect to the sum of the adsorption energies of isolated F4-TCNQ and isolated TTF.

nitrobenzene diazonium tetrafluoroborate. In a recent theoretical investigation,<sup>18</sup> we showed that lithium doping significantly increase the binding energy of free radicals to graphene as well as that of the azomethine ylides attached via the 1,3-dipolar cycloaddition. In the particular case of the addition of the hydroxyl radical, the C–OH bond dissociation energy was augmented three times. Tapia et al.<sup>19</sup> reported that potassium doping increase the hydrogen atom binding energy up to 82%. This value is in good agreement with the one we observed for hydrogen when lithium is used as doping agent.<sup>18</sup> The enhanced reactivity due to electron doping is not unexpected because the extra charge attracts the unpaired electrons of free radicals. Notwithstanding this fact, Huang et al.<sup>20</sup> came up with a surprising result: any type of doping will make the bonding between graphene and hydrogen kinetically more stable. They used a charge densities up to  $7.5 \times 10^{13} \text{ cm}^{-2}$ , which corresponds to almost one  $|e|$  for a  $5 \times 5$  graphene sheet and concluded that the effect of hole doping is higher than electron doping. In the case of hydrogen, it was reported that the binding energy increases from 20.8 to 27.7 kcal/mol (33%). This percentage is much smaller than the one computed by us (64%) and Tapia et al.<sup>19</sup> (82%).

The examples discussed above regarding the influence of charge doping on the reactivity of graphene have been limited to alkali atoms or artificial charges.<sup>17–21</sup> The use of organic molecules as dopants to modify the reactivity of graphene has been scarcely studied. At the same time, theoretical calculations have been applied to unravel the chemical and physical properties of graphene.<sup>18–46</sup> For this reason, we have performed a theoretical investigation on the chemical reactivity of graphene when the electron acceptor F4-TCNQ and the electron donor TTF are adsorbed onto graphene. As byproduct, we report one of the first determinations of the adsorption energies of these two molecules onto graphene, using van der Waals corrected density functional theory by means of the VDW-DF<sup>47</sup> M06-2X and M06-L<sup>48</sup> methods.

## 2. METHODS

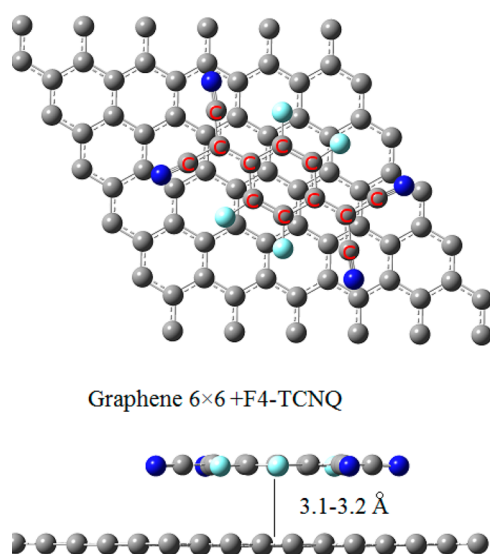
Density functional theory calculations were performed as implemented in Gaussian 2009<sup>49</sup> and SIESTA.<sup>50,51</sup> VDW-DF<sup>47</sup> calculations were carried out with SIESTA which performs self-consistent field (SCF) calculations using numerical basis sets. For this, we have selected the double- $\zeta$  basis set with polarization functions and fixed the orbital confining cutoff to 0.01 Ry (3.138 kcal/mol). The split norm used was 0.15. The DFT implementation in SIESTA can be prone to significant basis set superposition error (BSSE), even with relatively low degree of radial confinement.<sup>32</sup> To avoid this

problem, we used the counterpoise correction suggested by Boys and Bernardi.<sup>52</sup> In all cases, we employed relaxed structures to estimate the BSSE corrected binding energies, and we took monomer deformation energies into account. The interaction between ionic cores and valence electrons was described by the Troullier–Martins norm conserving pseudopotentials.<sup>53</sup> We have checked the convergence of the Mesh cutoff; using a value of 200 Ry, we obtained converged binding energies (within 0.1 kcal/mol). It is important to note that in our previous studies we performed methodology calibration against mesh cutoff and orbital confining cutoff values. By doing so, we were able to reproduce the results obtained without the use of pseudopotentials.<sup>18,25,27,31–37</sup> Geometry optimizations were carried out using the conjugate gradient algorithm until all residual forces were smaller than 0.01 eV/Å. To simulate infinite graphene sheets we used a  $6 \times 6$  supercell comprising 72 atoms. We optimized the unit cells along the *a*- and *b*-axes and while the *c*-axis was large enough to prevent interaction between adjacent sheets (25 Å). In all calculations the functional group was attached on the opposite side of the adsorbed molecule. The reason to do so is that we wanted to minimize the undesired chemical reactions that may occur between the adsorbed molecules and the fluorine/hydroxyl functional groups. We note that the single sided functionalization of graphene is possible nowadays. The unit cells were sampled using a  $30 \times 30 \times 1$  Monkhorst–Pack sampling, around 500 k-points, similar to the one used in our previous work about the chemical and electronic properties of doped graphene.<sup>18,25,27,31–37</sup> For the M06-L<sup>48</sup> calculations we used 1000 k-points and the ultrafine grid. The basis sets selected were the 6-31G\* and 6-311G\* ones.<sup>54</sup> Geometries were optimized with the 6-31G\* basis set, and single-point calculations were computed using the 6-311G\* basis set. Tight thresholds were employed for the Gaussian-based optimizations. Because M06-2X is more accurate than M06-L, we performed cluster model calculations for comparative purposes. A graphene flake terminated with hydrogen atoms and composed by 48 atoms was built. These calculations were intended to evaluate the performance of M06-L. For the cluster model calculations the correlation consistent cc-pVTZ and cc-pVQZ basis sets were also utilized.<sup>55</sup> The M06-2X/cc-pVQZ single-point calculations were conducted on the M06-2X/cc-pVTZ geometry. The M06-L and M06-2X results were not corrected for BSSE given that in a recent work<sup>56</sup> we have observed that this functional underestimates dispersion interactions. This finding is in line with the results obtained by Zhao and Truhlar<sup>57</sup> which indicated that for  $\pi$ – $\pi$  stacking complexes the error in the adsorption energies is 0.21 kcal/mol

if BSSE is not taken into account. However, it climbs to 0.39 kcal/mol if BSSE is added. Therefore, due to this fortuitous error cancellation, the BSSE uncorrected M06-L/6-31G\* values are very close to the B97-D results. For a detailed discussion about the error that can be expected from the M06-2X and M06-L calculations, the reader is referred to the work by Zhao and Truhlar. We note that the singlet close shell state of the nanocluster is unstable since the ground state is an open shell singlet. Yet, as we are interested in the interaction between graphene and the aforementioned organic molecules, the interaction employing the unstable close shell wave function is a better model than the open shell singlet. For the cluster model calculations, all stationary points were checked to be a minimum by calculating analytical vibrational frequencies. The Gaussian-based calculations were conducted with the ultrafine grid. Adsorption energies were calculated as  $E(\text{graphene}) + E(\text{adsorbed molecule}) - E(\text{graphene molecule ads})$ .

### 3. RESULTS AND DISCUSSION

**3.1. Adsorption of One and Two F4-TCNQ Molecules onto Graphene.** The structure of the graphene–F4-TCNQ complex is presented in Figure 1. This configuration is different



**Figure 1.** Optimized unit cell for the adsorption of F4-TCNQ onto graphene (top and side views) at the M06-L/6-31G\* level of theory (gray atoms: carbon atoms of graphene; gray atoms with a red C: carbon atoms of F4-TCNQ; blue atoms: nitrogens; cyan atoms: fluorines).

from that reported by Manna and Pati.<sup>11</sup> However, as we will discuss below, the charge transfer is similar. The most stable structure is in agreement with that reported by Zhang et al.<sup>13</sup> and Chi et al.<sup>16</sup> We have found that there are several configurations with comparable binding energy and similar charge transfer. At the VDW-DF/DZP level, the adsorption energy (AE) of F4-TCNQ is 29.4 kcal/mol. This value is very close to the one computed at the M06-L/6-31G\* level of theory, namely, 30.9 kcal/mol. However, when the basis set is increased to 6-311G\*, the AE is 36.0 kcal/mol. As can be seen, the agreement between both functionals is reasonable despite having very different formulations and implementations. On one hand, the VDW-DF calculations which use numerical basis sets and suffer from serious BSSE. In effect, the BSSE uncorrected VDW-DF adsorption energy is 60.4 kcal/mol. On the other hand, the M06-L/6-31G\* calculations which use Gaussian basis sets. For the sake of completeness, we performed LDA/DZP calculations. At this level, the AE is 21.1 kcal/mol, much lower than the aforementioned values, a result somewhat expected if we recall that LDA does not treat nonbonded interactions properly. Our values can be compared with those computed by Pinto et al.<sup>10</sup> and Manna et al.<sup>11</sup> at the LDA and PBE levels, respectively. The LDA result of ref 10 is 27.7 kcal/mol, about 6 kcal/mol larger than the LDA result reported here. Yet, it is 8.3 kcal/mol smaller than the M06-L/6-311G\* figure. The PBE AE of ref 11 is too high, with a value of 47.3 kcal/mol. Although the latter value was determined for TCNQ and we studied F4-TCNQ, it is still about 50% larger than our interaction energy. Such large value at the PBE level is unrealistic because this functional works tremendously bad for nonbonded interactions. For example, in the case of the benzene dimer the interaction is repulsive. Therefore, such large AE can be attributed only to the fact that in ref 11 the authors used SIESTA and did not include basis set superposition error, which was close to 30 kcal/mol, in our case. Another interesting comparison can be made with the results obtained by Haldar et al.<sup>58</sup> for a related molecule, TCNQ. This compound was adsorbed in two configurations: (a) a configuration similar to the one obtained by us (Figure 1); (b) a configuration in which the hexagon of TCNQ is directly above and hexagon of graphene, but the carbon atoms of TCNQ are rotated 15° with respect to those belonging to the underneath hexagon. At the BLYP-D3 level structure (a) was more stable by 0.6 kcal/mol, but DFTB-D suggested that (b) is more stable by 0.2 kcal/mol. Our M06-L/6-31G\* calculations performed for F4-TCNQ indicated that (a) is more stable by 0.6 kcal/mol. Thus, as mentioned above, there are several orientations with similar energy available for F4-TCNQ to be adsorbed onto graphene.

**Table 2.** Binding Energies Determined for the Addition of Fluorine and OH to Graphene and Doped Graphene

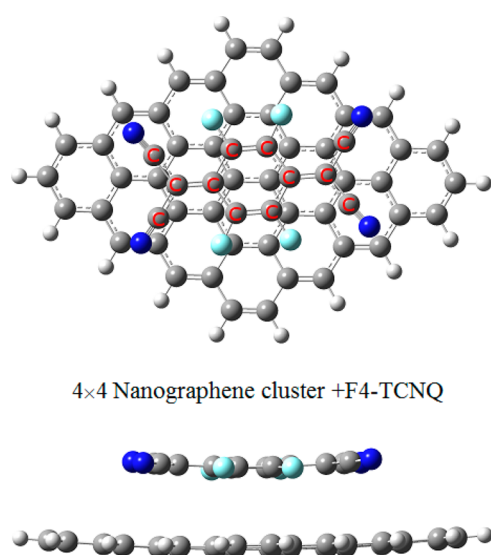
	F			OH		
	graphene	graphene–F4-TCNQ	graphene–TTF	graphene	graphene–F4-TCNQ	graphene–TTF
VDW-DF/DZP	30.3	33.0		9.4	13.4	
M06-L/6-31G*	29.6	31.4	32.3	10.4	12.5	12.6
M06-L/6-311G* <sup>a</sup>	28.7	31.7	31.8	10.8	12.9	13.3
M06-2X/6-31G*	35.3	36.2		19.5	20.6	20.1
M06-2X/6-311G*	33.7	34.4	34.2	20.3	21.3	20.8
M06-2X/cc-pVTZ	34.4	35.2	35.1	17.7	18.7	
M06-2X-cc-pVQZ <sup>b</sup>	34.0	35.5	34.6	17.2	18.8	

<sup>a</sup>Single-point calculation at the M06-L/6-31G\* geometry. <sup>b</sup>Single-point calculation at the M06-2X/cc-pVQZ geometry.



The charge transferred from graphene to TCNQ was found to be 0.43 and 0.40  $e^-$  with VDW-DF/DZP and M06-L/6-311G\*, respectively, in line with the values reported in previous works.<sup>10–12</sup> It is well-known that Mulliken charges have a peculiar basis set dependence. For this reason, we evaluated the charge transfer at the M06-L/6-311G\* level. At this level of theory, the charge received by F4-TCNQ is 0.35  $e^-$ , nearly the same observed with the smaller basis set. Finally, we note that when F4-TCNQ is adsorbed onto graphene, the overall composite has a small magnetic moment of 0.25  $\mu_B$  at the VDW-DF/DZP level of theory. The analysis of the magnetic moment on each atom indicated that for the graphene–F4-TCNQ composite, the 0.25  $\mu_B$  figure, comes almost exclusively from the adsorbed molecule while the contribution of graphene is close to zero. This came as a surprise since Manna et al.<sup>11</sup> reported that the graphene remains nonmagnetic when TCNQ is adsorbed onto graphene. The reason for such a discrepancy may be related to the fact that in ref 11 the PBE method was used.

The M06-L functional is a good choice for periodic systems because of its local character. However, it is less accurate than M06-2X. Because the latter includes exact exchange, the periodic calculations are extremely complex. Therefore, we used a nanographene cluster with the edges saturated with H atoms to study the adsorption of F4-TCNQ. The complex is presented in Figure 2. At the M06-2X/6-31G\* level of theory,



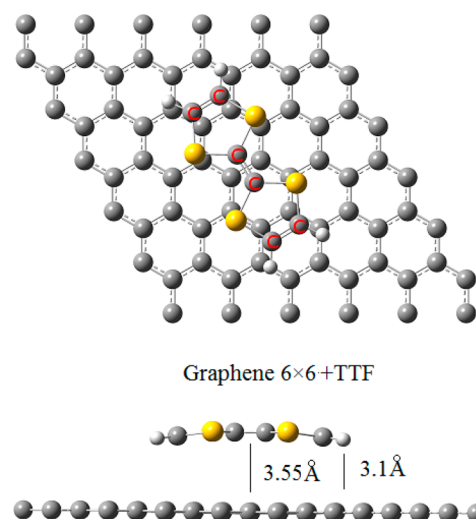
**Figure 2.** Optimized structure for the complex between the 4 × 4 graphene nanocluster and F4-TCNQ (top and side views) at the M06-2X level of theory (gray atoms: carbon atoms of the nanographene cluster; gray atoms with a red C: carbon atoms of F4-TCNQ; blue atoms: nitrogens; cyan atoms: fluorines).

the AE of F4-TCNQ on the hydrogen-terminated nanographene cluster is 29.4 kcal/mol, in good agreement with the M06-L result, determined for infinite graphene. When M06-L is used to study the adsorption of F4-TCNQ onto the nanographene cluster, it was found that the AE is 32.9 kcal/mol, 3.5 kcal/mol larger than the M06-2X result. For these nanographenes it is possible to use very large basis sets. When M06-2X/cc-pVQZ calculations are performed at the M06-2X/cc-pVTZ geometry, the AE is only 25.7 kcal/mol, in reasonable agreement with the periodic results. Regarding the charge transferred when using the cluster model, it was 0.22  $e^-$  at the

M06-2X/6-31G\* level and  $-0.19 e^-$  when the cc-pVTZ basis set was employed. This value is almost 50% lower as compared with the one computed for graphene, a reasonable result if we consider that the cluster has only 48 carbon atoms and the graphene layer is infinite with a density of adsorbates of 1 F4-TCNQ molecule per  $6 \times 6$  unit cell. We have tested that the separation between the adsorbates is large enough to minimize their interaction. Moreover, graphene does not have a band gap while the cluster model has a sizable HOMO–LUMO gap. Charges derived from the natural population analysis (NPA) were similar to those obtained from the Mulliken study. In effect, at the M06-2X/cc-pVTZ level the charge of F4-TCNQ is  $-0.2 e^-$ . When two F4-TCNQ molecules are adsorbed on opposite sides of the nanographene cluster, the adsorption energy decreases to 27.5 kcal/mol per molecule, at the M06-L/6-31G\* level of theory; the charge transferred to each molecule is 0.17  $e^-$ , which is 0.05  $e^-$  smaller as compared with the single adsorption. In contrast, the total charge of the nanographene cluster is higher (+0.34).

In recent work it has been shown that the formation of the  $C_{60}$ –corannulene complex is endergonic ( $\Delta G_{298}^\circ$ : +3.5 kcal/mol).<sup>59</sup> This result is a consequence of the strong entropy penalty that is necessary to bring these two molecules close. For graphene–F4-TCNQ, a similar phenomenon is expected. We used the  $C_{48}H_{18}$  cluster to estimate the gas phase association energy. At the M06-2X/6-31G\* level of theory  $\Delta G_{298}^\circ$  was  $-14.5$  kcal/mol, which suggests that the adsorption of F4-TCNQ onto graphene is feasible from a thermodynamic standpoint.

**3.2. Adsorption of TTF onto Graphene.** The structure of this complex is presented in Figure 3. The structure is different



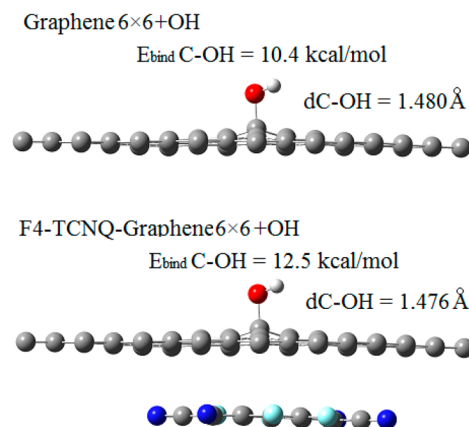
**Figure 3.** Optimized unit cell for the adsorption of TTF onto graphene (top and side views) at the M06-L/6-31G\* level of theory (gray atoms: carbon atoms of graphene; gray atoms with a red C: carbon atoms of TTF; white atoms: hydrogen; yellow atoms: sulfur).

than the one found by Manna et al.<sup>11</sup> but similar to that presented by Zhang et al.;<sup>13</sup> i.e., the central CC bond of TTF is perpendicular to a CC bond of graphene. The interaction between TTF and graphene is roughly half the value computed for F4-TCNQ. In effect, the VDW-DF/DZP and M06-L/6-31G\* results yielded AE values of 15.5 and 15.9 kcal/mol, respectively. When the M06-L/6-311G\* method is used, the AE is a bit larger, namely, 20.1 kcal/mol. At the LDA/DZP

level, the AE is 6.8 kcal/mol, 3 times lower than in the case of F4-TCNQ, a proof of the inadequacy of LDA for studying these weakly interacting complexes. In contrast with the results by Manna et al.,<sup>11</sup> we did not observe any charge transfer between TTF and graphene at the VDW-DF and M06-L levels. It is worth noting though that according to these authors, it is only 0.1  $e^-$ . The AE determined using the nanographene cluster and the M06-2X/6-31G\* method is 15.1 kcal/mol, in reasonable accord with the aforementioned values. Also, the AE determined using cluster models and M06-L is quite close, amounting to 14.3 kcal/mol. The AE determined using the cc-pVQZ is 14.3 kcal/mol. Consistently with our periodic calculations, we found that there is no significant charge transferred from TTF to graphene, just +0.02 as indicated by Mulliken and NPA analysis. As observed for F4-TCNQ, our AE for TTF is significantly lower than previously reported.<sup>11</sup> Again, the discrepancy is rooted in the lack of BSSE for the PBE calculations performed with SIESTA.<sup>11</sup> Finally, the free energy change for complexation was evaluated using the M06-2X/6-31G\* method and the graphene nanocluster. At the latter level of theory  $\Delta G_{298}^\circ$  was  $-2.5$  kcal/mol. Although this value is negative, it is much closer to thermodynamical neutrality than the one computed for F4-TCNQ.

**3.3. Simultaneous Adsorption of TTF and F4-TCNQ onto Graphene.** The simultaneous adsorption of TTF and F4-TCNQ on opposite sides of the graphene sheet was investigated to check if the presence of TTF can alter the charge transfer process to F4-TCNQ. At the M06-L/6-31G\* level of theory, the combined AE is 47.1 kcal/mol. This value is 0.32 kcal/mol larger than the sum of the AE of F4-TCNQ and TTF. When the 6-311G\* basis set is employed, the simultaneous adsorption of both molecules yields an AE that is 1.1 kcal/mol larger than the sum of the separated AE. The VDW-DF/DZP calculations support the M06-L/6-31G\* results, but the simultaneous adsorption increases the AE by 4.4 kcal/mol. The magnetic moment of the whole composite is 0.15  $\mu_B$ . This value is smaller as compared with that determined for the F4-TCNQ-graphene complex. The reduction is due to the presence of TTF on the other side of the sheet. The presence of TTF increases the amount of charge received by F4-TCNQ. In effect, the charges of TTF and F4-TCNQ are +0.29 and  $-0.57$   $e^-$  at the M06-L/6-31G\* level, respectively. When the 6-311G\* basis set is used, the charges are smaller, +0.17 and  $-0.38$   $e^-$  for TTF and F4-TCNQ, respectively. Thus, for infinite graphene we conclude that the presence of F4-TCNQ enables the charge transfer from TTF to graphene, something that was not observed without the electron acceptor molecule. The cluster model calculations performed at the M06-2X/cc-pVQZ level of theory indicated that the AE of the TTF-graphene-F4-TCNQ system is 41.7 kcal/mol. This value is 1.8 kcal/mol larger than the sum of the AE of TTF and F4-TCNQ. Also, the charge transfer is improved when both molecules are simultaneously adsorbed.

**3.4. Reactivity of Graphene with F4-TCNQ Adsorbed.** The binding energy (BE) of OH onto graphene is 10.5 kcal/mol and the C–OH distance is 1.480 Å, both computed at the M06-L/6-31G\* level of theory. The structure of the F4-TCNQ-graphene + OH complex is presented in Figure 4. When F4-TCNQ is adsorbed on the opposite side, the OH bond distance decreases to 1.476 Å and the total interaction energy of the system is 43.4 kcal/mol. This value is 2.1 kcal/mol larger than the sum of the AE of F4-TCNQ and the BE of graphene–OH. This was a puzzling finding because the

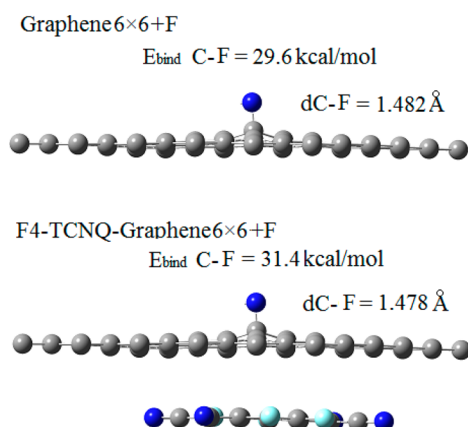


**Figure 4.** Optimized unit cell for the addition of OH to graphene (top) and to F4-TCNQ-graphene at the M06-L/6-31G\* level of theory (gray atoms: carbon atoms; blue atoms: nitrogens; cyan atoms: fluorines; red atom: oxygen; white atom: hydrogen).

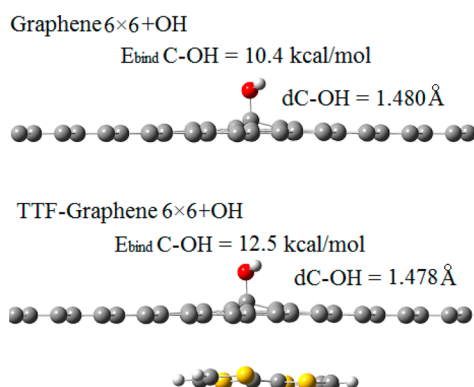
presence of F4-TCNQ induces hole doping of graphene hence reducing the number of electrons available for the hydroxyl radical. The attachment of OH increases the amount of charge transferred to F4-TCNQ, which now is 0.47  $e^-$ , nearly 0.1  $e^-$  larger than that observed for the F4-TCNQ complex. When the same analysis is performed employing a larger basis set (6-311G\*), the outcome is quite similar; the presence of F4-TCNQ increases the C–OH bond energy by 2.1 kcal/mol, and the charge of F4-TCNQ is  $-0.42$   $e^-$ . The results obtained with the VDW-DF and LDA functionals are in good agreement with the M06-L ones as the simultaneous presence of OH and F4-TCNQ increases the interaction energy by 4.0 and 1.0 kcal/mol, respectively. Despite using a nanographene cluster, the results obtained with M06-2X/6-31G\* support the enhancement of the C–OH binding energy by the presence of F4-TCNQ. This statement holds true even when cc-pVQZ basis sets are employed. However, there is one difference between the periodic and finite calculations; the charge of F4-TCNQ is slightly smaller (0.07  $e^-$  less) as compared with F4-TCNQ free of OH. We attribute this variation to the finite character of the nanographene cluster.

In order to verify whether the results obtained for the hydroxyl radical are maintained for other reactants, the addition of fluorine was studied. The complex between F4-TCNQ and graphene-F is presented in Figure 5. At the M06-L/6-31G\* level of theory, it was found, in a similar fashion to OH, that the presence of F4-TCNQ decreases the C–F bond distance from 1.482 to 1.478 Å. The total interaction energy is 62.3 kcal/mol, 1.8 kcal/mol larger than the sum of the EA of F4-TCNQ and BE of graphene-F (29.7 kcal/mol). At the M06-L/6-311G\* level the enhancement of the C–F binding energy is even larger, namely, 3.1 kcal/mol. The outcome of the VDW-DF calculations is similar: the presence of F4-TCNQ increases the interaction energy of the system by 2.7 kcal/mol. In the same vein, the cluster model calculations with all basis set support the aforementioned findings. In light of all these results, we conclude that hole doping of graphene with F4-TCNQ increases the BE of radicals onto graphene.

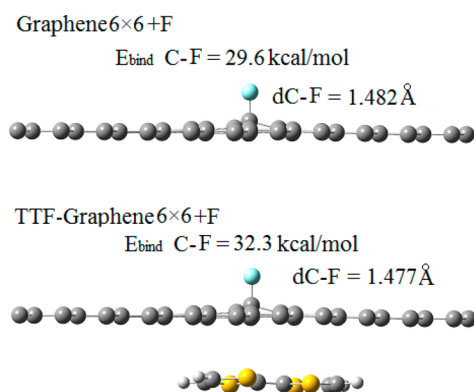
**3.5. Reactivity of Graphene with TTF Adsorbed.** The addition of OH and fluorine is favored by the presence of TTF. The structures are presented in Figures 6 and 7 for F and OH, respectively. For the addition of OH, the C–OH is reduced from 1.480 to 1.478 Å, while the interaction of the system is 2.2



**Figure 5.** Optimized unit cell for the addition of fluorine to graphene (top) and to F4-TCNQ-graphene (bottom) at the M06-L/6-31G\* level of theory (gray atoms: carbon atoms; blue atoms: nitrogens; cyan atoms: fluorines).



**Figure 6.** Optimized unit cell for the addition of OH to graphene (top) and to TTF-graphene (bottom) at the M06-L/6-31G\* level of theory (gray atoms: carbon atoms; yellow atoms: sulfur; red atom: oxygen; white atom: hydrogen).



**Figure 7.** Optimized unit cell for the addition of fluorine to graphene (top) and to TTF-graphene (bottom) at the M06-L/6-31G\* level of theory (gray atoms: carbon atoms; cyan atoms: fluorines; white atom: hydrogen; yellow atoms: sulfur).

kcal/mol higher than the sum of the AE of TTF and the BE of OH, all results being at the M06-L/6-31G\* level of theory. The M06-L/6-311G\* results predicted an even larger enhancement of the BE, namely 2.5 kcal/mol. For fluorine, the effect is comparable as the total interaction energy of the system increases by 2.7 kcal/mol and the C–F bond distance is

contracted by 0.005 Å. Although charge donation from TTF in the TTF–graphene complex was not observed, for the interaction between functionalized graphene with OH or F, it was found that TTF displays a positive charge of +0.16 and +0.1 for fluorine and hydroxyl functionalization at the M06-L/6-31G\* level, respectively. We note that at the M06-L/6-311G\* level the charge of TTF is more positive, +0.23 and +0.27, when OH and F are attached, respectively. The larger charge transfer from TTF to graphene when fluorine is attached to graphene as compared with hydroxyl is consistent with the larger electronegativity of fluorine. We note that the charge of fluorine is the same with and without TTF adsorbed onto graphene. Therefore, the charge donated by TTF to graphene is not transferred to fluorine. The cluster model calculations support the finding obtained when periodic conditions were imposed. However, as observed for F4-TCNQ, the magnitudes of the enhancements of the C–X BE (X = F, OH) are smaller than those obtained using infinite models.

#### 4. CONCLUSIONS

The M06-L and VDW-DF dispersion corrected density functionals were applied to investigate the chemical reactivity of electron-doped and hole-doped graphene. The electron acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) and the electron donor tetrathiafulvalene (TTF) were selected as doping agents. The reactions considered were the addition of fluorine atoms and hydroxyl radicals. The following are deemed the most important conclusions of the present work:

1. The adsorption of F4-TCNQ and TTF increased the reactivity of graphene toward the addition of fluorine atoms and hydroxyl radicals.
2. The adsorption energy of F4-TCNQ onto graphene is 29.4 and 36.0 kcal/mol at the VDW-DF and M06-L/6-311G\* levels of theory, respectively, whereas for TTF the adsorption energy is 15.5 and 20.1, kcal/mol, respectively, at the same levels of theory. All results obtained with infinite models and using the VDW-DF and M06-L functionals are supported by cluster model calculations performed with the M06-2X method. The adsorptions of F4-TCNQ and TTF are exergonic, but the free energy change computed for TTF is closer to thermodynamic neutrality.
3. When TTF and F4-TCNQ are simultaneously adsorbed on opposite sides of the graphene sheet, the amount of charge accepted by F4-TCNQ and donated by TTF is increased. Therefore, dual doping is a useful tool to expand, even to a greater extent, the possibilities to tune the molecular properties of graphene.
4. The results show that the reactivity of graphene can be altered by the adsorption of organic molecules that can donate or withdraw electrons from graphene. Although the changes that we observed are small (in the 10–15% range), we consider that they could become larger if further work is devoted to synthesize better electron donors and acceptors which would allow for larger charge transfer so as to modify the chemical reactivity of graphene.



## ■ AUTHOR INFORMATION

## Corresponding Author

\*E-mail pablod@fq.edu.uy; Tel 0059899714280; Fax 00589229241906.

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The author thanks PEDECIBA Quimica for financial support.

## ■ REFERENCES

- (1) Chen, W.; Chen, S.; Qi, D. C.; Gao, X. Y.; Wee, A. T. S. Surface Transfer p-Type Doping of Epitaxial Graphene. *J. Am. Chem. Soc.* **2007**, *129*, 10418–10422.
- (2) Subrahmanyam, K. S.; Voggu, R.; Govindaraj, A.; Rao, C. N. R. A Comparative Raman Study of the Interaction of Electron Donor and Acceptor Molecules with Graphene Prepared by Different Methods. *Chem. Phys. Lett.* **2009**, *472*, 96–98.
- (3) Varghese, N.; Ghosh, A.; Voggu, R.; Ghosh, S.; Rao, C. N. R. Selectivity in the Interaction of Electron Donor and Acceptor Molecules with Graphene and Single-Walled Carbon Nanotubes. *J. Phys. Chem. C* **2009**, *113*, 16855–16859.
- (4) Barja, S.; Garnica, M.; Hinarejos, J. J.; Vazquez de Parga, A. L.; Martín, N.; Miranda, R. Self-organization of Electron Acceptor Molecules on Graphene. *Chem. Commun.* **2010**, *46*, 8198–8200.
- (5) Coletti, C.; Riedl, C.; Lee, D. S.; Krauss, B.; Patthey, L.; von Klitzing, K.; Smet, J. H.; Starke, U. Band Structure Engineering of Epitaxial Graphene on SiC by Molecular Doping. *Phys. Rev. B* **2010**, *81*, 235401.
- (6) Kaminska, I.; Das, M. R.; Coffinier, Y.; Niedziolka-Jonsson, J.; Woisel, P.; Opallo, M.; Szunerits, S.; Boukherroub, R. Preparation of Graphene/Tetrathiafulvalene Nanocomposite Switchable Surfaces. *Chem. Commun.* **2012**, *48*, 1221–1223.
- (7) Zhang, Z.; Huang, H.; Yang, X.; Zang, L. Tailoring Electronic Properties of Graphene by  $\pi$ - $\pi$  Stacking with Aromatic Molecules. *J. Phys. Chem. Lett.* **2011**, *2*, 2897–2905.
- (8) Lauffer, P.; Emtsev, K. V.; Graupner, R.; Seyller, T.; Ley, L. Molecular and Electronic Structure of PTCDA on Bilayer Graphene on SiC(0001) Studied With Scanning Tunneling Microscopy. *Phys. Status Solidi B* **2008**, *245*, 2064–2067.
- (9) Park, J.; Jo, S. B.; Yu, Y.-J.; Kim, Y.; Yang, J. W.; Lee, W. H.; Kim, H. H.; Hong, B. H.; Kim, P.; Cho, K.; et al. Single-Gate Bandgap Opening of Bilayer Graphene by Dual Molecular Doping. *Adv. Mater.* **2012**, *24*, 407–411.
- (10) Pinto, H.; Jones, R.; Goss, J. P.; Briddon, P. R. p-type Doping of Graphene With F4-TCNQ. *J. Phys.: Condens. Matter* **2009**, *21*, 402001.
- (11) Manna, A. K.; Pati, S. K. Tuning the Electronic Structure of Graphene by Molecular Charge Transfer: A Computational Study. *Chem.—Asian J.* **2009**, *4*, 855–860.
- (12) Yong, Y.; Song, B.; He, P. Stability and Magnetism of Tetracyanoethylene Adsorbed on Substitutionally Doped Graphene. *J. Appl. Phys.* **2012**, *111*, 083713.
- (13) Zhang, Y.-H.; Zhou, K.-G.; Xie, K.-F.; Zeng, J.; Zhang, H.-L.; Peng, Y. Tuning The Electronic Structure and Transport Properties of Graphene by Noncovalent Functionalization: Effects of Organic Donor, Acceptor and Metal Atoms. *Nanotechnology* **2010**, *21*, 065201.
- (14) Lu, Y. H.; Chen, W.; Feng, Y. P.; He, P. M. Tuning the Electronic Structure of Graphene by an Organic Molecule. *J. Phys. Chem. B* **2009**, *113*, 2–5.
- (15) Wuest, J. D.; Rochefort, A. Strong Adsorption of Aminotriazines on Graphene. *Chem. Commun.* **2010**, *46*, 2923–2925.
- (16) Chi, M.; Zhao, Y.-P. First Principle Study of the Interaction and Charge Transfer Between Graphene and Organic Molecules. *Comput. Mater. Sci.* **2012**, *56*, 79–84.
- (17) Fan, X.; Nouchi, R.; Tanigaki, K. Effect of Charge Puddles and Ripples on the Chemical Reactivity of Single Layer Graphene Supported by SiO<sub>2</sub>/Si Substrate. *J. Phys. Chem. C* **2011**, *115*, 12960–12964.
- (18) Denis, P. A. Chemical Reactivity of Lithium Doped Monolayer and Bilayer Graphene. *J. Phys. Chem. C* **2011**, *115*, 13392–13398.
- (19) Tapia, A.; Acosta, C.; Medina-Esquivel, R. A.; Canto, G. Potassium Influence in the Adsorption of Hydrogen on Graphene: A Density Functional Theory Study. *Comput. Mater. Sci.* **2011**, *50*, 2427–2432.
- (20) Huang, L. F.; Ni, M. Y.; Zhang, G. R.; Zhou, W. H.; Li, Y. G.; Zheng, X. H.; Zeng, Z. Modulation of the Thermodynamic, Kinetic, and Magnetic Properties of the Hydrogen Monomer on Graphene by Charge Doping. *J. Chem. Phys.* **2011**, *135*, 064705.
- (21) Huang, L. F.; Cao, T. F.; Gong, P. L.; Zeng, A.; Zhang, C. Tuning the Adatom-surface and Interadatom Interactions in Hydrogenated Graphene by Charge Doping. *Phys. Rev. B* **2012**, *86*, 125433.
- (22) Jiang, D.; Sumpter, B. G.; Dai, S. How Do Aryl Groups Attach to a Graphene Sheet? *J. Phys. Chem. B* **2006**, *110*, 23628–23632.
- (23) Georgakilas, V.; Bournlos, A. B.; Zboril, R.; Steriotis, T. A.; Dallas, P.; Stubos, A. K.; Trapalis, C. Organic Functionalisation of Graphenes. *Chem. Commun.* **2010**, 1766–1768.
- (24) Quintana, M.; Spyrous, K.; Grzelczak, M.; Browne, W. R.; Rudolf, P.; Prato, M. Functionalization of Graphene via 1,3-Dipolar Cycloaddition. *ACS Nano* **2010**, *4*, 3527–3533.
- (25) Denis, P. A.; Iribarne, F. *Int. J. Quantum Chem.* **2010**, *110*, 1764–1771.
- (26) Cao, Y.; Houk, K. N. Computational Assessment of 1,3-dipolar Cycloadditions to Graphene. *J. Mater. Chem.* **2011**, *21*, 1503–1508.
- (27) Denis, P. A.; Iribarne, F. The 1,3 Dipolar Cycloaddition of Azomethine Ylides to Graphene, Single Wall Carbon Nanotubes, and C60. *J. Phys. Chem. C* **2011**, *115*, 195–203.
- (28) Suggs, K.; Reuven, D.; Wang, X.-Q. Electronic Properties of Cycloaddition-Functionalized Graphene. *J. Phys. Chem. C* **2011**, *115*, 3313–3317.
- (29) Zhong, X.; Jin, J.; Li, S.; Niu, Z.; Hu, W.; Li, R.; Ma, J. J. Aryne Cycloaddition: Highly Efficient Chemical Modification of Graphene. *Chem. Commun.* **2010**, *46*, 7340–7342.
- (30) Ghaderi, N.; Peressi, M. First-Principle Study of Hydroxyl Functional Groups on Pristine, Defected Graphene, and Graphene Epoxide. *J. Phys. Chem. C* **2010**, *114*, 21625–21630.
- (31) Denis, P. A. Iribarne, On the Hydrogen Addition to Graphene. *F. J. Mol. Struct.: THEOCHEM* **2009**, *907*, 93–103.
- (32) Denis, P. A. Density Functional Investigation of Thioepoxidated and Thiolated Graphene. *J. Phys. Chem. C* **2009**, *113*, 5612–5619.
- (33) Denis, P. A.; Faccio, R.; Mombru, A. W. Is It Possible to Dope Single-Walled Carbon Nanotubes and Graphene with Sulfur? *ChemPhysChem* **2009**, *10*, 715–722.
- (34) Denis, P. A. Band Gap Opening of Monolayer and Bilayer Graphene Doped With Aluminium, Silicon, Phosphorus, and Sulphur. *Chem. Phys. Lett.* **2010**, *492*, 251–257.
- (35) Denis, P. A. When Noncovalent Interactions are Stronger Than Covalent Bonds: Bilayer Graphene Doped With Second Row Atoms, Aluminum, Silicon, Phosphorus and Sulphur. *Chem. Phys. Lett.* **2011**, *508*, 95–101.
- (36) Denis, P. A.; Iribarne, F. Cooperative Behavior in Functionalized Graphene: Explaining the Occurrence of 1,3 Cycloaddition of Azomethine Ylides onto Graphene. *Chem. Phys. Lett.* **2012**, *550*, 111–117.
- (37) Denis, P. A.; Iribarne, F. Thiophene Adsorption on Single Wall Carbon Nanotubes and Graphene. *J. Mol. Struct.: THEOCHEM* **2010**, *957*, 114–119.
- (38) Chandrachud, P.; Pujari, B. S.; Haldar, S.; Sanyal, B.; Kanhere, D. K. A Systematic Study of Electronic Structure From Graphene to Graphene. *J. Phys.: Condens. Matter* **2010**, *22*, 465502.
- (39) Al-Aqtash, N.; Vasiliev, I. Ab Initio Study of Carboxylated Graphene. *J. Phys. Chem. C* **2009**, *113*, 12970–12975.
- (40) Dai, J.; Yuan, J.; Giannozzi, P. Gas Adsorption on Graphene Doped With B, N, Al, and S: A Theoretical Study. *Appl. Phys. Lett.* **2009**, *95*, 232105.



- (41) Dai, J.; Yuan, J. Modulating the Electronic and Magnetic Structures of P-doped Graphene by Molecule Doping. *J. Phys.: Condens. Matter* **2010**, *22*, 225501.
- (42) Ao, Z. M.; Yang, J.; Li, S.; Jiang, Q. Enhancement of CO Detection in Al Doped Graphene. *Chem. Phys. Lett.* **2008**, *461*, 276–279.
- (43) Ao, Z. M.; Yang, J.; Li, S.; Jiang, Q. Thermal Stability of Interaction Between the CO Molecules and the Al Doped Graphene. *Phys. Chem. Chem. Phys.* **2009**, *11*, 1683–1687.
- (44) Gong, S. J.; Sheng, W.; Chu, J. H. First-Principles Investigation of Bilayer Graphene With Intercalated C, N or O Atoms. *J. Phys.: Condens. Matter* **2010**, *22*, 245502.
- (45) Wang, F. T.; Chen, L.; Tian, C. J.; Meng, Y.; Wang, Z. G.; Zhang, R. Q.; Jin, M. X.; Zhang, P.; Ding, D. J. Interactions Between Free Radicals and a Graphene Fragment: Physical Versus Chemical Bonding, Charge Transfer, and Deformation. *J. Comput. Chem.* **2011**, *32*, 3264–3268.
- (46) Ivanovskaya, V. V.; Zobelli, A.; Teillet-Billy, D.; Rougeau, N.; Sidis, V.; Briddon, P. R. Hydrogen Adsorption on Graphene: a First Principles Study. *Eur. Phys. J. B* **2010**, *76*, 481.
- (47) Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Phys.* **2006**, *125*, 194101.
- (48) Dion, M.; Rydberg, H.; Schroder, E.; Langreth, D. C.; Lundqvist, B. I. Van der Waals Density Functional for General Geometries. *Phys. Rev. Lett.* **2004**, *92*, 246401.
- (49) Gaussian 09, Revision A.1: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian, Inc.: Wallingford, CT, 2009.
- (50) Soler, J. M.; Artacho, E.; Gale, J. D.; Garcia, A.; Junquera, J.; Ordejon, P.; Sanchez-Portal, D. The SIESTA Method for Ab Initio Order-N Materials Simulation. *J. Phys.: Condens. Matter* **2002**, *14*, 2745–2779.
- (51) Ordejon, P.; Artacho, E.; Soler, J. M. Self-Consistent Order-N Density-Functional Calculations for Very Large Systems. *Phys. Rev. B* **1996**, *53*, R10441–R10444.
- (52) Boys, F. S.; F. Bernardi, F. The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. *Mol. Phys.* **1970**, *19*, 553–566.
- (53) Troullier, N.; Martins, J. L. Efficient Pseudopotentials for Plane-Wave Calculations. *Phys. Rev. B* **1991**, *43*, 1993–2006.
- (54) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
- (55) Dunning, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron Through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (56) Denis, P. A. Theoretical Investigation of the Stacking Interactions Between Curved Conjugated Systems and Their Interaction with Fullerenes. *Chem. Phys. Lett.* **2011**, *516*, 82–87.
- (57) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main group Thermochemistry, Thermochemical Kinetics, Non-covalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of four M06-class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215.
- (58) Haldar, S.; Kolar, M.; Sedlak, R.; Hobza, P. Adsorption of Organic Electron Acceptors on Graphene-like Molecules: Quantum Chemical and Molecular Mechanical Study. *J. Phys. Chem. C* **2012**, *116*, 25328.
- (59) Zhao, Y.; Truhlar, D. G. Computational Characterization and Modeling of Buckyball Tweezers: Density Functional Study of Concave–convex  $\pi\cdots\pi$  Interactions. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2813–2818.