

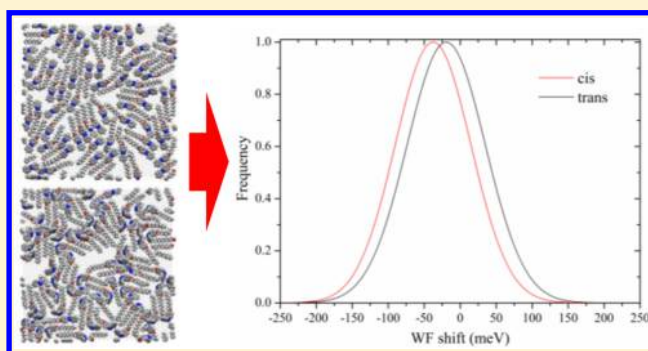
# Combined Molecular Dynamics and Density Functional Theory Study of Azobenzene–Graphene Interfaces

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## Supporting Information

**ABSTRACT:** The electronic properties of graphene can be tuned in a dynamic way from physical adsorption of molecular photoswitches. Here, we first investigate the formation of 4-(decyloxy)azobenzene molecular monolayers on a single graphene layer through molecular dynamics (MD) simulations and assess the associated change in work function (WF) at the density functional theory (DFT) level. We show that the major contribution to the WF shift arises from electrostatic effects induced by the azobenzene electric dipole component normal to graphene and that the conformational distribution of the molecular switches in either their trans or cis forms can be convoluted into WF distributions for the hybrid systems. We next use this strategy to build a statistical ensemble for the work functions of graphene decorated with fluorinated azobenzene derivative designed to maximize the change in WF upon photoswitching. These findings pave the way to the possible use of photoswitchable graphene-based hybrid materials as optically controlled memories for light-assisted programming and high-sensitive photosensors.



## 1. INTRODUCTION

The holy grail in nanotechnology consists of the design of multifunctional structures that combine in a synergetic way the properties of their individual components. To reach this purpose, functional molecular units able to express specific response functions are essential. For about 30 years, a large variety of supramolecular systems that exhibit complex functions and that react to external stimuli have been widely explored.<sup>1–4</sup> The discovery of graphene and its outstanding electronic properties has triggered vivid interest for graphene-based hybrid materials, where chemisorption or physisorption of properly designed atoms or small molecules provides a simple mean to tune or add new functionality to the 2D layer. Besides substitution with heteroatoms,<sup>5</sup> doped graphene layers can be generated by chemically grafting electron-rich or electron-poor molecules.<sup>6,7</sup> Though this approach offers the advantage that stable hybrid structures are formed, the honeycomb structure of graphene is disrupted, and as a consequence, its electronic and optical properties are altered. On the other hand, in the case of physisorption, the noncovalent interactions between graphene and small molecules preserve the  $\pi$ -conjugated structure of the former, yet the reversibility of the interaction can lead to the desorption of the molecules from the surface.

Among the vast variety of different possible functionalizations of graphene, the modulation of its electronic properties through the physisorption of light-responsive molecules has attracted much interest motivated by the numerous potential implications for relevant processes in optoelectronic applica-

tions, such as collection, conversion, and storage of solar energy.<sup>8–11</sup> Because of the high change in response upon photoswitching from their trans to cis configuration,<sup>12</sup> azobenzene derivatives are the candidates of choice to design new hybrid graphene-based photoswitching materials with enhanced optoelectronic and transport properties.

In this paper, the formation of a 4-(decyloxy)azobenzene (see Figure 1) monolayer on a graphene layer is investigated by molecular dynamics (MD) simulations. The change in work function due to the configurational switch of the azobenzene molecules is then analyzed via density functional theory (DFT) calculations, and the results are convoluted into a WF distribution. Finally, we use this strategy to study the WF shift of a fluorinated azobenzene derivative.

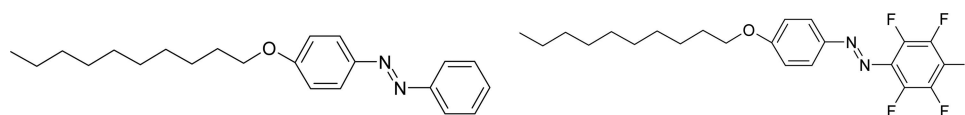
## 2. METHODOLOGY

**MD Calculations.** All molecular modeling simulations have been performed with the version 4.5.5 of the GROMACS molecular modeling package<sup>13</sup> using a modified version of the OPLSAA force field developed for azobenzenes,<sup>14,15</sup> which is known to well reproduce  $\pi$ - $\pi$  interactions.<sup>16</sup> The simulations have been conducted in vacuum and at room temperature in the NVT ensemble (constant Number of particles, Volume, and Temperature), and the Nose-Hoover thermostat has been used to control the temperature. The linear constraint solver

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**Figure 1.** Structures of the two different azobenzene molecules studied, 4-(decyloxy)azobenzene (left) and fluorinated 4-(decyloxy)azobenzene (right) in their trans conformation. Hydrogen atoms are not shown for clarity.

(LINCS) method has been applied to all molecular bonds to restrain them to their force field equilibrium length, allowing the use of a time step for the simulations of 2 fs. The orthorhombic simulation box measures  $10 \times 10 \times 10$  nm, and periodic boundary conditions (PBC) are used. A cutoff of 1.5 nm is applied for both van der Waals and electrostatic interactions (plain cutoff). The graphene layer upon which the monolayers are modeled has been considered as an infinite rigid-body frozen in space to reduce the computational cost.

**DFT Calculations.** The work function (WF) shift upon physisorption of the photochromic molecules on graphene has been investigated at the density functional theory (DFT) level of theory using the SIESTA3 software.<sup>17,18</sup> The local density approximation (LDA) in combination with the Ceperley–Alder exchange–correlation functional<sup>19–21</sup> has been used. The LDA approach has been demonstrated to correctly reproduce interfacial electronic structure and charge transfer for different donor/acceptor molecules physisorbed on graphene or other metals, especially when periodic boundary conditions are applied.<sup>22,23</sup> We further stress that the main contribution to the modulation in the work function of the hybrid materials is driven by the ground-state dipoles of the photoswitches in their respective conformation at the graphene surface and that this is only very weakly method sensitive, as proven by the good agreement between force field and DFT/LDA results (as shown in Tables S3–S4). To further strengthen the use of the LDA functional, we calculated the dipole moment of representative conformations (the same as for the WF analysis) at the MP2 level of theory and found a good agreement with LDA (data reported in Table S5). The valence electrons are described by the DZP basis set<sup>19</sup> while the core electrons are described adopting the Troullier–Martins pseudopotentials. A mesh cutoff of 500 Ry and a k-sampling of (35, 10, 1) in the Monkhorst–Pack scheme<sup>24</sup> was used. With this setup, the work function of the clean graphene layer matches the experimental value of 4.82 eV.<sup>25</sup>

Two main contributions are responsible for the total shift in the work function ( $\Delta\Phi$ ): the first arises from the dipole moment of the molecular backbone, named hereafter molecular contribution ( $\Delta\Phi_{\text{SAM}}$ ), and the second from the interfacial electronic reorganization upon physisorption, namely, the charge transfer contribution ( $\Delta\Phi_{\text{CT}}$ ):

$$\Delta\Phi = \Delta\Phi_{\text{SAM}} + \Delta\Phi_{\text{CT}} \quad (1)$$

$\Delta\Phi_{\text{SAM}}$  has been estimated here by computing the electrostatic potential profile across the molecules while keeping the geometry frozen. The  $\Delta\Phi_{\text{CT}}$  contribution is then calculated by subtracting  $\Delta\Phi_{\text{SAM}}$  from  $\Delta\Phi$ .

In the Helmholtz model,<sup>26,27</sup> the molecular contribution  $\Delta\Phi_{\text{SAM}}$  is directly proportional to the molecular dipole along the axis normal to the surface,  $\mu_{\perp}$ , and is inversely proportional to the surface area per adsorbed molecule A:<sup>28</sup>

$$\Delta\Phi_{\text{SAM}} = e\mu_{\perp}/\epsilon_0 A \quad (2)$$

with  $\epsilon_0$  the vacuum permittivity. The calculated electronic density is then used to build the plane-averaged electrostatic potential normal to the graphene layer; in this way, it is possible to obtain a direct estimation of the shift in the work function by comparing the potential on the bare and on the SAM-covered side of the graphene surface.

### 3. RESULTS AND DISCUSSION

**1. 4-(Decyloxy)azobenzene.** *a. Monolayer Formation.* For both the trans and cis forms of 4-(decyloxy)azobenzene molecules (hereafter called azobenzene), we are interested in modeling a dense, amorphous monolayer of molecules lying mostly flat on the surface, so as to maximize their interaction with graphene. To model such a monolayer, we devised a molecular deposition procedure on the basis of molecular dynamic simulations. We present here the analysis performed to individuate the most stable self-assembly for trans-azobenzene molecules, while the analysis for the other systems are reported in the Supporting Information (SI). The devised protocol follows a one-by-one molecular deposition scheme: an azobenzene molecule is inserted in the modeling box at a random position and orientation in such a way that its center of mass is located 1.5 nm above the graphene plane (and within the cutoff range for the molecule–graphene nonbonding interaction). A 100 ps MD at a temperature of 300 K is then performed in order to let the molecule adsorb and diffuse on the graphene layer; the same procedure is repeated for each adsorption event. The final assemblies have been further equilibrated with a 6 ns long MD. The densest monolayer obtained using this approach contains 80 molecules per unit cell; if the molecular deposition process is continued, a bilayer starts to form. The densest monolayer has an estimated surface coverage of 98.6% and has been calculated considering the surface contact area analysis (SCA) for the whole SAM in a unit cell, averaged over time (see SI). We assume that the true assembly is the one that maximizes the interactions between the molecules and the graphene while ensuring a high graphene coverage (>90%). Hence, we compute and compare the energies of three dense monolayers containing 80, 72, and 64 molecules. To compare the results between the different assemblies, we compute binding energy expressed per molecule and the assembly surface interaction energy. Here, the binding energy per molecule ( $E_{\text{bin}}/N$ ), which estimates the quality of the intermolecular interactions taking place between the azobenzene molecules in the monolayer, is calculated as the difference between the average internal energy of the assembly (in which  $N$  molecules interact together) on the surface over the whole trajectory ( $E_{\text{pot}}^{\text{sys}}$ ) and the sum of the noninteracting molecules on the surface ( $\sum_{i=1}^N E_{\text{pot}}^i$ ), normalized by the number of molecules forming the monolayer ( $N$ ):

$$E_{\text{bin}}/N = (E_{\text{pot}}^{\text{sys}} - \sum_{i=1}^N E_{\text{pot}}^i)/N \quad (3)$$

This energy only quantifies how favorable (or unfavorable) it is for an azobenzene molecule to be part of a self-assembly of a

given molecular density. Because this energy does not consider how strongly the assembly is interacting with the graphene, we calculate the assembly surface interaction energy per molecule, which is simply the average van der Waals energy per molecule ( $\langle E_{\text{vdW}} \rangle / N$ ), normalized by the number of molecules forming the monolayer ( $N$ ). The results are reported in Table 1,

**Table 1. Summary of Structural and Energetic Characterizations of Dense Trans and Cis Azobenzene Monolayers**

# molecules $N$	$\langle \text{SCA} \rangle$ $\text{nm}^2$	% coverage	$\langle E_{\text{vdW}} \rangle / N$ $(\text{kJ mol}^{-1} \text{ molecule}^{-1})$	$E_{\text{bin}} / N$ $(\text{kJ mol}^{-1} \text{ molecule}^{-1})$
AZO Trans				
64	1.90	91.7	-131.9	-43.9
72	1.85	97.3	-128.2	-48.0
80	1.72	98.6	-117.7	-55.5
AZO Cis				
64	1.72	82.1	-117.1	-39.1
72	1.69	90.5	-117.3	-43.0
80	1.64	95.7	-112.2	-43.9

together with the average molecule–graphene surface contact area ( $\langle \text{SCA} \rangle$ ) for the molecules in the assemblies and the estimated graphene coverages. The  $\langle \text{SCA} \rangle$  is obtained as the average of the azobenzene–graphene SCA for each single molecule physisorbed on the graphene sheet, along the whole trajectory.

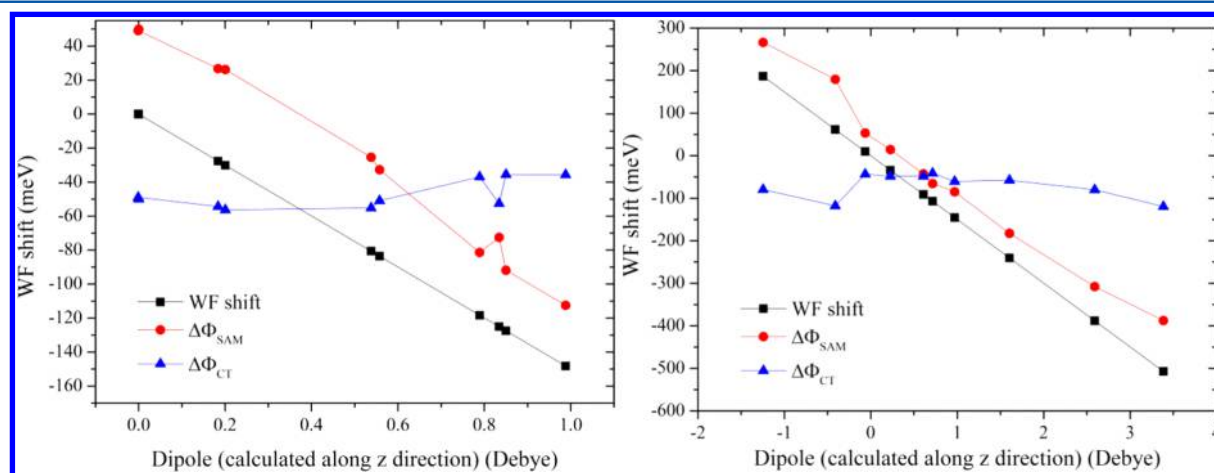
From the structural and energetic analysis performed on the three trans azobenzene monolayers, the most stable one is that composed of 64 molecules: for this monolayer, the calculated binding energy per molecule ( $E_{\text{bin}}/N$ ) is  $11.7 \text{ kJ mol}^{-1}$  and  $4.1 \text{ kJ mol}^{-1}$  smaller than that obtained for the assemblies of 80 and 72 molecules, respectively. On the other hand, the average magnitude of the molecule–graphene interactions ( $\langle E_{\text{vdW}} \rangle / N$ ) is  $14.3 \text{ kJ mol}^{-1}$  and  $3.8 \text{ kJ mol}^{-1}$  larger than that obtained for the 80 and 72 molecule assemblies, respectively. To explain these results, we compare the  $\langle \text{SCA} \rangle$  for the molecules in the different assemblies to the footprint for the ideal case of a single molecule of azobenzene laying flat on the graphene surface. This footprint, calculated with the same method used to obtain the  $\langle \text{SCA} \rangle$ , is  $1.99 \text{ nm}^2$ , which is larger than the  $\langle \text{SCA} \rangle$

calculated for the molecules in the assemblies. This indicates that the molecules in the denser monolayers are tilted on the surface rather than being fully flat on the graphene surface, and the more tilted they are, the less favorable are their interactions with the graphene surface. Because the energetic balance between  $\langle E_{\text{vdW}} \rangle / N$  and  $E_{\text{bin}}/N$  is more favorable for the monolayer composed of 64 molecules, we consider this one as the true monolayer, which is used in the rest of our work (Figures S1 and S2).

From a similar analysis (SI), we selected cis azobenzene, fluorinated trans azobenzene, and fluorinated cis azobenzene monolayers of 72, 64, and 72 molecules, respectively.

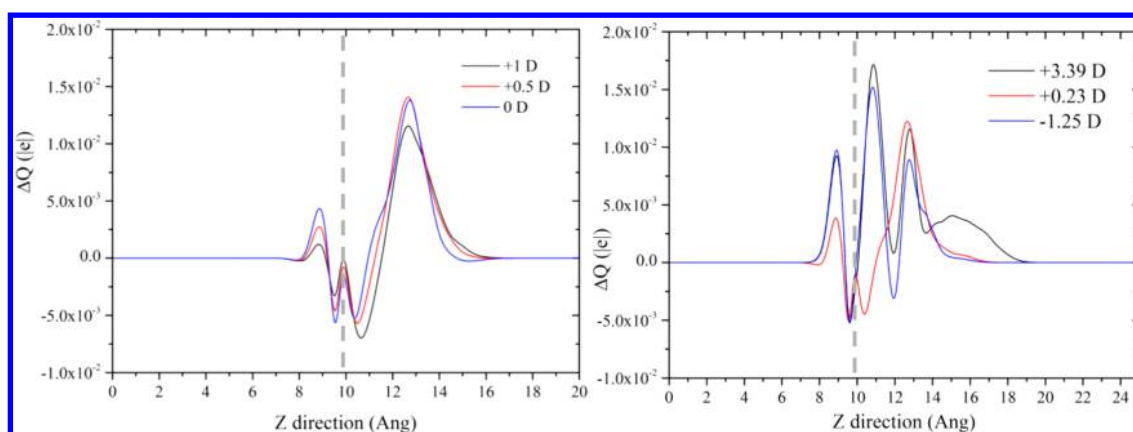
**b. Origin of the Work Function Shift.** Out of the azobenzene monolayers predicted from the MD simulations, we randomly picked 10 molecules that are representative of the dipole moment distributions (see after) and calculated to which extent such molecules affect the work function of graphene at the DFT level (representative conformations for both the trans and cis isomers are reported in Figure S3 and S4). The plane-averaged potential profiles for the different conformations of the trans isomer show an increase of the WF shift with increasing the dipole moment (along the  $z$  direction) of the SAM–graphene system, ranging from zero when the dipole is null, to  $\sim -150 \text{ meV}$  for a dipole of  $\sim 1 \text{ D}$ . A similar behavior is obtained for the cis isomer, but with a larger window range; in particular, the WF shift ranges from positive values up to  $190 \text{ meV}$  for a negative dipole of  $-1.2 \text{ D}$  to a negative value of  $-500 \text{ meV}$  for a positive dipole value of  $3.4 \text{ D}$  (see Figure 2).

To disentangle the contributions to this shift arising from the charge transfer from the graphene and from the intrinsic dipole moment of the molecule, the computed potential profile of the free SAM was also analyzed. For the trans form, the molecular contribution ( $\Delta\Phi_{\text{SAM}}$ ) follows the same trend as the WF shift, going from positive values for negative dipoles (of the system) to negative values for positive dipoles, while the charge transfer ( $\Delta\Phi_{\text{CT}}$ ) contribution is almost constant for all the conformers studied, with an average value of  $\sim -50$  ( $\sim -70$ )  $\text{meV}$  for the trans (cis) isomer (Figure 2). The shift of the work function is hence driven mostly by the molecular contribution, which is sensitive to molecular conformation, while the charge transfer is smaller, irrespective of the azobenzene conformation. Interestingly, the two contributions add up constructively for positive

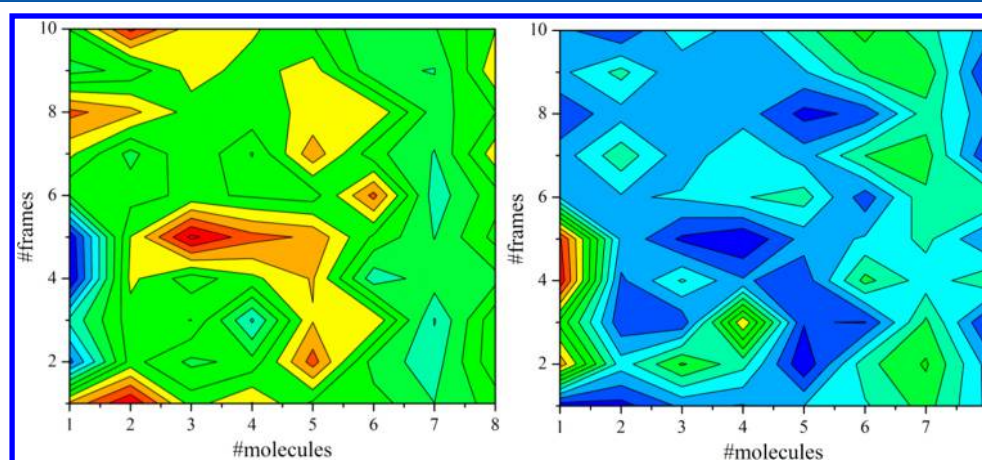


**Figure 2.** WF shift (black line) for the trans (left) and cis (right) isomers of selected molecules extracted from MD snapshots of the azobenzene–graphene system, as a function of the normal component of the total dipole moment of the system. The molecular contribution ( $\Delta\Phi_{\text{SAM}}$ , red line) and the charge transfer ( $\Delta\Phi_{\text{CT}}$ , blue line) are also reported.





**Figure 3.** Charge analysis for the trans (left) and cis (right) isomers of different conformers selected from the SAM dipole moments distribution, along the  $z$  axis of the cell. The gray dotted line points to the graphene sheet.



**Figure 4.** 2D map of the distribution of the  $z$  component of the dipole moment for the selected molecules in the selected frames (left) and the distance between the nitrogen atom of the azobenzene molecules from graphene (right) for the cis isomer. Color code for the left map: positive dipole values (red) to negative dipole values (blue). Color code for the right map: nitrogen and oxygen atoms close to the graphene layer (blue) to farther from the graphene (red).

dipole values, while the opposite is true for negative values of the dipole moment.

For the cis conformations, the molecular dipole moments evolve from  $-1.78$  to  $2.58$  D in the gas-phase geometry (calculated in a large unit cell to avoid intermolecular interactions) while the corresponding values range from  $-1.25$  to  $3.48$  D in the SAM. A similar trend is found for trans conformations, with molecular dipoles ranging from  $-0.33$  to  $0.75$  D in gas phase and from  $0$  to  $0.99$  D in the SAM.

In Figure 3, we show plane-integrated charge distributions versus out-of-plane distance for representative structures of the trans and cis isomers. In particular, conformations with small, medium, and large ground-state state molecular dipole moments were selected to check for possible correlation with the interfacial charge reorganization. Interestingly, for the trans isomer, the accumulation of partial charge does not depend on the dipole moment, with a (small) partial positive charge ranging from  $1.2 \cdot 10^{-2}$  to  $1.5 \cdot 10^{-2}$  |e| present on the adsorbed molecule and the compensating negative charge on graphene. This thus indicates that the graphene is slightly n-doped, in agreement with the WF analysis. The same analysis for the different conformers of the cis isomer leads to the same conclusion, that is, n-doping of graphene, with a partial charge

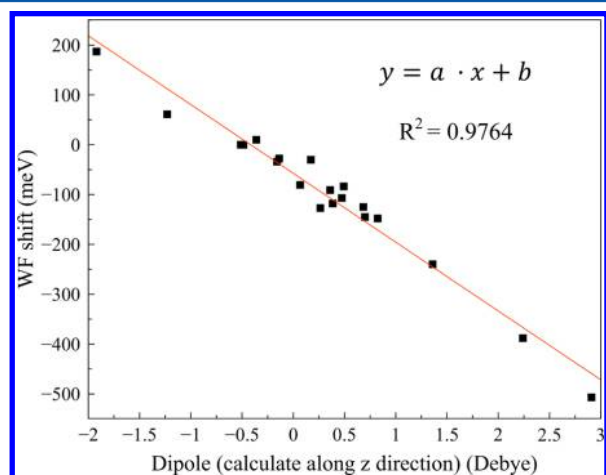
transfer from the molecule to graphene in the range  $0.5 \cdot 10^{-2}$  to  $1.8 \cdot 10^{-2}$  |e|, depending on the molecular conformation.

*c. Work Function Ensemble Distribution.* To build an ensemble distribution of the work function, we first calculate the  $z$  (graphene normal) component of the molecular dipole moment for all the 64 (72) molecules over the whole trajectory of the MD simulation (1 ns long, 500 frames). Out of this, we randomly extracted 8 molecules in 10 frames and recalculated the dipole moment along the  $z$  component (normal to graphene surface) at the DFT level, for both trans and cis isomers. As shown in Tables S3–S4, a very good agreement is found between the force field and the DFT results. We next further analyzed the correlation between the direction of the dipole moment and the orientation of the head of the azobenzene molecule on the graphene layer for the cis isomer and found the coexistence of two populations: in the first case, the phenyl ring is pointing toward the graphene layer while in the second case it is pointing away from the graphene layer (see Figure S3).

In particular, when the  $z$  component of the dipole moment has a high positive value (red in Figure 4, left), the distance to graphene of the azobenzene N and O atoms is larger (dark blue in Figure 4, right); hence, the head of the azobenzene molecule is pointing toward the graphene layer. For large and negative

dipoles (dark blue in Figure 4, left), the corresponding distance is smaller; hence, the head of the azobenzene molecule is pointing away from the graphene layer. Thus, we can correlate differences in the positioning and conformation of the azobenzene molecules physisorbed on graphene with their dipole moment, an essential parameter to understand changes in the WF of graphene induced by physisorption. The same analysis for the trans isomer does not bring much insight as the trans molecules lay almost flat on the graphene surface. Hence, the correlation is more subtle and might be related to the arrangement of either the oxygen atom or the alkyl chain with respect to the graphene surface.

When comparing the DFT and MD results, we find that the DFT WF shift follows a close to linear relationship with the dipole moments of the molecules (along  $z$ ) as calculated from MD, Figure 5.



**Figure 5.** Correlation between WF shift (from DFT) and dipole distribution (obtained by MD simulations). The solid red line is a linear fit;  $a = -138.04$  and  $b = -57.46$ .

With the validation made in the previous section, it is now possible to build the distribution of the WF shift from the distribution of the dipole moment calculated at the MD level. The MD dipole moments reported in Figure 6 (left) follow a Gaussian like distribution, with values spanning a  $-1$  to  $+1.5$  D

window, with average and standard deviation of 0.14 and 0.39 (0.27 and 0.38) D for the trans (cis) isomers, respectively.

The distribution of the WF shift  $P(\Delta\Phi_{\text{SAM}})$  is then computed as

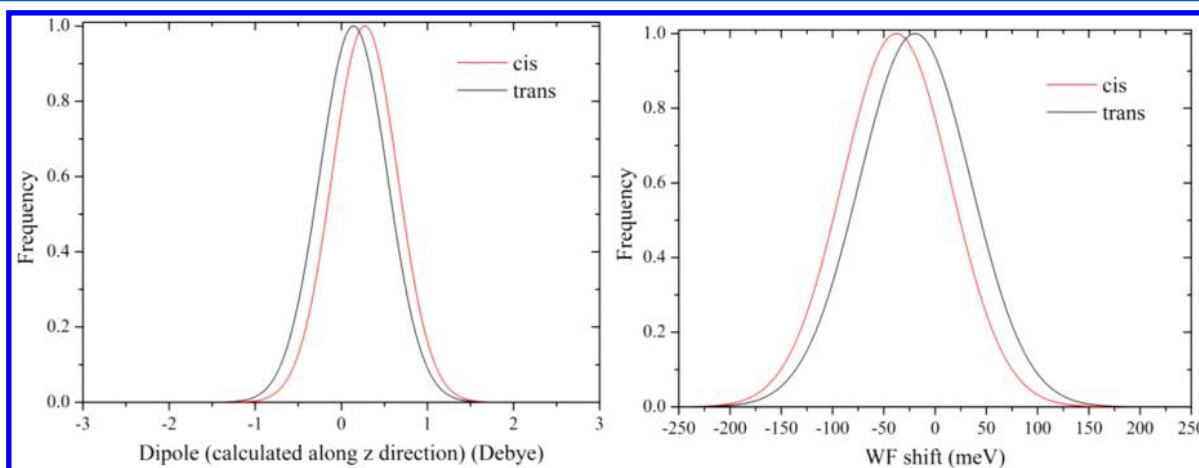
$$P(\Delta\Phi_{\text{SAM}}) = \Delta\Phi_{\text{SAM}}(\mu) \times P(\mu) \quad (4)$$

where  $\Delta\Phi_{\text{SAM}}(\mu)$  is the linear fit of the correlation between the WF shift associated with the molecular dipole and the dipole moment calculated at the MD level and  $P(\mu)$  is the dipole distribution obtained at the MD level. The WF shift distribution (including the  $\Delta\Phi_{\text{CT}}$  contribution) is shown in Figure 6 (right). The average and standard deviation values for the WF are  $-20$  and  $54$  ( $-38$  and  $53$ ) meV for the trans (cis) isomer, respectively. Hence, the WF shift associated with the switch from the trans to the cis isomer is  $\Delta\Phi_{\text{t-c}} \sim -18 \pm 50$  meV.

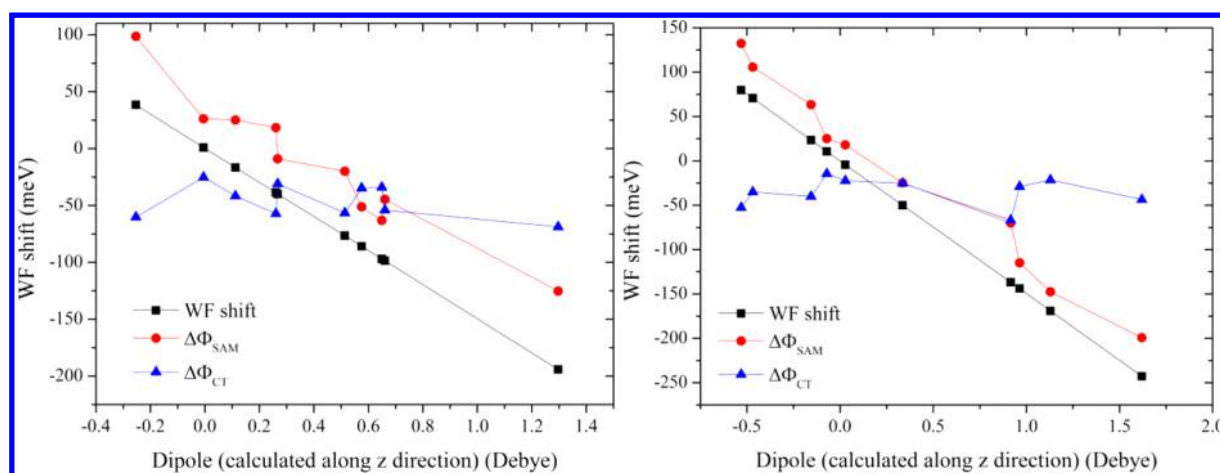
The higher work function shift calculated for the cis form is fully consistent with experimental data<sup>29</sup> (obtained after sonication of graphite with azobenzene intercalation), yet with the predicted trans to cis shift being smaller than the measured experimental value of about  $-70$  meV. We speculate that this discrepancy is at least partly due to neglecting the solvent in the simulations and the approximations used to build the adlayer.

**2. Fluorinated Azobenzene.** Next, we designed a new molecule presenting fluorination over the head phenyl ring (Figure 1, right) and built a dense monolayer. Here also, we find a similar increase of the WF shift with molecular dipole, with values ranging from 38 meV when the dipole is  $-0.25$  D to  $-194$  meV for a dipole of 1.30 D. A similar behavior is obtained for the cis isomer, but with a larger window range; in particular, the WF shift ranges from positive values up to 80 meV for negative dipole of  $-0.53$  D to negative value of  $-243$  meV for positive dipole value of 1.62 D (see Figure 7).

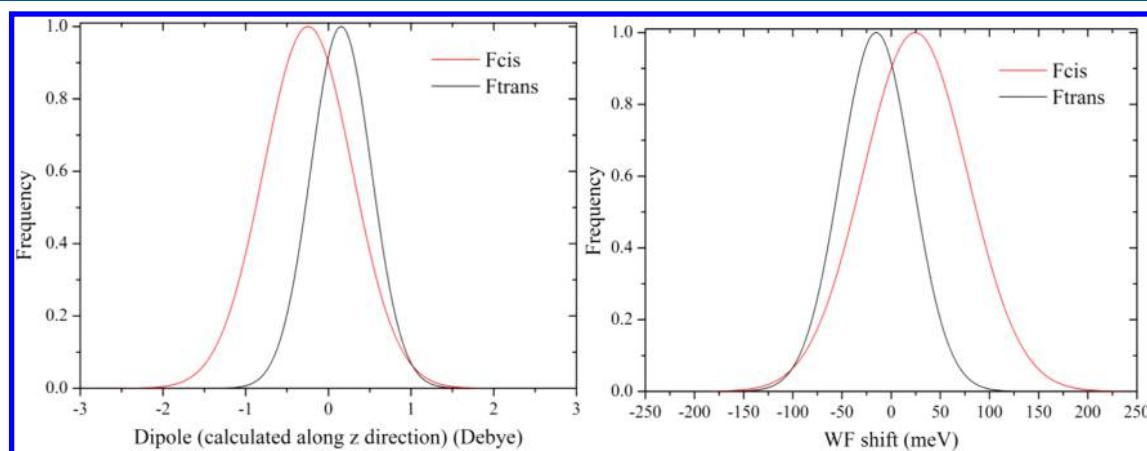
Again, as for the nonfluorinated counterpart, the molecular contribution ( $\Delta\Phi_{\text{SAM}}$ ) is following the same trend as the WF shift and is the main contribution to the change in the WF. The charge-transfer ( $\Delta\Phi_{\text{CT}}$ ) contribution is almost constant for all conformers sampled along the MD trajectories, with an average value of 35 (45) meV for the trans (cis) isomer, thus smaller than the nonfluorinated molecules (Figure 7). This can be traced back to the lowest partial negative charge over the graphene layer compared to the nonfluorinated azobenzene



**Figure 6.** Normalized fit of the dipole distribution of azobenzene obtained by MD simulations (left) and normalized distribution of the WF shift (right).



**Figure 7.** WF shift (black line) for the trans (left) and cis (right) isomers of selected molecules extracted from MD snapshots of the fluorinated azobenzene–graphene system, as a function of the normal component of the total dipole moment of the system. The molecular contribution ( $\Delta\Phi_{\text{SAM}}$ , red line) and the charge transfer ( $\Delta\Phi_{\text{CT}}$ , blue line) are also reported.



**Figure 8.** Normalized fit of the dipole distribution of fluorinated azobenzene obtained by MD simulations (left) and normalized distribution of the WF shift (right).

SAM, which is expected on the basis of the electron-withdrawing character of the fluorine substituents (see SI for more details). Here also, the dipole moment of the molecules primarily entails the shift in the work function; the main difference is the direction of the dipole moment of the fluorinated azobenzene molecules, opposite to that in the nonfluorinated molecules.

The procedure described earlier was then used to analyze the fluorinated monolayer. As in the nonfluorinated case, we find a close to linear relation between the WF shift obtained by DFT and the dipole moment calculated at the MD level (see SI). This allows us to convolute the dipole distribution into a WF shift distribution. The distribution of the dipole moment along the  $z$  direction ranges from  $-1$  ( $-2$ ) to  $1.5$  D for the trans (cis) isomer, and it peaks at  $0.15 \pm 0.37$  D for the trans isomer. The fluorination has a more profound impact on the cis isomer, with a larger shift of the dipole moments toward negative values and peak values at  $-0.25 \pm 0.54$  D, Figure 8 (left). The higher standard deviation for the cis isomer denotes a broader dipole distribution with respect to the trans.

The convoluted WF shift distribution ranges from  $-150$  to  $100$  meV for the trans isomer, with a maximum probability at  $-15 \pm 36$  meV (see Figure 8, right). A broader distribution is obtained for the cis isomer, ranging from  $-150$  to  $200$  meV and

peaking at  $+25 \pm 53$  meV. As expected, the fluorination plays an important role in the WF shift only for the cis isomer, where a large  $z$  component of the dipole moment is predicted, while for the trans isomer the dipole is weaker; in both cases (with and without fluorination), both the dipole and the WF shift distribution are very similar. This leads to a WF shift induced by photoisomerization of  $\Delta\Phi_{t-c} \sim +40 \pm 45$  meV.

#### 4. CONCLUSIONS

In summary, the structural and electronic properties of graphene–azobenzene hybrid systems have been investigated by means of molecular dynamics coupled to ab initio simulations. From MD simulations, we predict the formation of an amorphous monolayer of azobenzene derivatives physisorbed on a graphene sheet and extract a statistical distribution of the dipole moment along the normal to the graphene sheet. The subsequent study of representative molecules from the MD ensemble by DFT calculations provides a direct link between the change in WF of different azobenzene conformers and their dipole moments, as sampled along the MD runs. For both isomers of (fluorinated) azobenzenes, the CT contribution is negative and constantly independent of the molecular conformation and positioning on the graphene layer; the SAM contribution is larger and drives



the overall shift in the WF when going from the trans to the cis isomer. The convolution of the work function shift  $\Delta\Phi(\mu)$  and the dipole distribution  $P(\mu)$  leads to a WF shift distribution  $P(\Delta\Phi)$ . In this way, it is possible to obtain a statistical distribution of the WF shift depending on the orientation of the trans and cis isomers on graphene. The calculated  $\Delta\Phi_{t-c}$  of  $\sim -18 \pm 50$  meV is in reasonable agreement with the experimental Kelvin probe force microscopy (KPFM) data of  $-70$  meV, with in particular a higher WF shift predicted for the cis isomer. Moreover, the fluorination of the azobenzene head leads to a  $\Delta\Phi_{t-c} = +40 \pm 45$  meV, with a reverse sign with respect to the nonfluorinated azobenzene molecule. Hence, the physisorption of azobenzene molecules on a graphene monolayer, while keeping the electronic structure of graphene largely unaffected, leads to (small) changes in the WF induced by the molecular component of the dipole moment. We propose to use such a molecular strategy, namely, designing molecules with large (changes of) ground-state dipoles, to tune the WF of graphene over a broader range. This example of a hybrid system can be used as a building stone in the fabrication of more complex responsive devices and paves the way to future applications, such as photosensors and optically controllable memory switches.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b00393.

Analysis of the solvent accessible surface area (SASA), surface coverage and energy analysis for the (fluorinated) azobenzene derivative at the MD level of theory, for both trans and cis isomers. Comparison between the dipole moments obtained by MD and the DFT calculations for both isomers of the (fluorinated) azobenzene derivative, charge analysis for selected molecules, representation of different conformations of the SAM, and correlation between WF shift and dipole distribution for fluorinated azobenzene conformers

(PDF)

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### Notes

The authors declare no competing financial interest.

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