Molecular adsorption of iminotriazine derivatives on graphene

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Abstract
The non-covalent functionalisation of graphene is the method of choice for modulating the electronic and chemical properties of graphene materials without markedly disturbing the electron density in the final structures. In this respect, different aromatic and amphiphilic molecules have been reported, and their interactions with graphene materials have been studied in order to design catalysts, sensors or other electronic devices. The interactions between a set of iminotriazine derivatives and graphene have been studied using state of the art first principle calculations, which were corroborated with experimental data. An effective non-covalent interaction of the systems has been demonstrated and, although the variation of the electronic properties of the starting graphene is minimal, the electronic properties of some iminotriazines changed significantly.

1. Introduction

The discovery of graphene has opened up a new area of research to exploit the unique properties of this material. Graphene has outstanding mechanical and thermal properties and a characteristic electronic structure [1, 2], which defies its characterisation between semiconductors and metals. Scientists have learned to modulate the properties of graphene either through covalent or non-covalent functionalisation [3, 4].

Graphene can be functionalised by addition reactions, thereby transforming the hybridisation of carbon from sp2 to sp3. Covalent modification disrupts the electronic distribution of graphene, thus modifying the physical properties and producing a dramatic decrease in charge carrier mobility [5, 6]. In contrast, non-covalent functionalisation perturbs the electron density to a lesser extent and allows finer modulation of the electronic and chemical properties of graphene. The most important supramolecular interactions in non-covalent functionalisation are dispersion forces (e.g. van der Waals) and π−π interactions.

London dispersion forces or van der Waals interactions are weaker than π−π interactions and affect atoms nearby. Since graphene is hydrophobic in nature, it can interact with amphiphilic molecules such as surfactants, ionic liquids or macromolecules. The hydrophobic interactions with surfactants have been used to improve the stability of dispersions in water [7]. Ionic interactions are produced by ionic groups on the graphene surface, mainly carboxylate and alkoxide groups. In this way, interactions with amphiphilic molecules enhance the stability of graphene dispersions in solvents [8].

Graphene interacts effectively with π-conjugated molecules through π−π interactions. These materials can be applied to surface transfer doping [9], bandgap opening (for FET applications) [10], increased film conductivity (as an alternative to ITO) or increased sensitivity of graphene-based molecular sensors [11], in redox reactions (water splitting reaction) [12], green catalysis and photocatalysis [13, 14], environmental chemistry [15], biomedicine and biosensors [16] and specific drug-delivery in biological tissue [17, 18].

π − π interactions have been successfully used in the exfoliation of graphite and the stabilisation of graphene in solution. They have also been used for applications such as the formation of composite functional materials, like polymer composites with improved mechanical, electrical, and thermal responses.
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Figure 1. (a) Iminotriazines (IT1–IT4). (b) Top view: structural features of adsorbed ITx molecules on graphene; (c) Lateral view: average distance between iminotriazines and graphene.

[19], and also in drug delivery and biomedical applications [20]. However, π-π interactions have a notable effect in altering properties such as photoluminescence [21], UV–vis spectra [22], hydrophobicity, hydrophilicity and stability [23].

We have previously studied the interaction between 1,3,5-triazines and graphene, and we used this interaction for the exfoliation of graphene induced mechanochemically and in solvent-free conditions [24, 25]. 1,3,5-Triazines are heterocyclic compounds with numerous applications in supramolecular chemistry due to their ability to form supramolecular networks through non-covalent interactions such as hydrogen bonding, aromatic stacking interactions and electrostatic and charge transfer processes [26, 27].

In the present work, we report an experimental and computational study focused on how the modification of the 1,3,5-triazine moiety affects its interaction with graphene and whether such interactions can modulate the electronic properties of graphene [27–29]. In this regard, we have used Density Functional Theory (DFT) as a method that has been used and continues to help with the understanding of how supramolecular networks interacts with graphene [30]. The study of the effect of molecular adsorption on the graphene structure is of particular interest since it has been shown that this process could lead to bandgap opening [31, 32].

2. Results and discussion

DFT has become a standard technique for describing electronic systems at the atomic level. However, DFT fails to describe interactions like hydrogen bonds or molecular adsorption on the surface through van der Waals (vdW) interactions [33–36]. Fortunately, improvements have been made to this method in recent years, and these have provided a better description of interactions in the framework of DFT [37–43]. DFT has been used in combination with an empirical model that takes into account van der Waals interactions [44–48] to study the influence of molecular self-assembly on graphene and the resulting electronic modifications. Recently, we described the formation of supramolecular networks with the aim of analysing the competition between intermolecular interactions and adsorption energies on a graphene monolayer [49]. This study enabled the role of melamine in the macroscopic process of graphene exfoliation by ball-milling to be understood. The interaction between nitrogen-rich benzene derivatives and graphene or finite-type graphene has previously been reported elsewhere [50].

2.1. Theoretical interaction of graphene with iminotriazines

Our initial aim was to understand, from a theoretical point of view, the types of interaction that can be expected between graphene and the following iminotriazines: 6-[4-(benzylideneamino)phenyl]-1,3,5-triazine-2,4-diamine (IT1), 6-[4-[(4-dimethylamino)benzylidene]aminophenyl]IT-1,3,5-triazine-2, 4-diamine (IT2), 6-[4-[(4-methoxybenzylidene)amino]phenyl]-1,3,5-triazine-2,4-diamine (IT3) and 6-4-[(2-thienylmethylene)amino]phenyl]-1,3,5-triazine-2,4-diamine (IT4), respectively (figure 1).

We sought information about how these iminotriazine derivatives could act as graphite exfoliation agents or if these molecules simply act as doping agents and modify the electronic properties of graphene.

Based on our experience in the theoretical study of the exfoliation of graphite with melamine [49], density functional theory (DFT-D) was used to investigate the interactions of IT1 to IT4 with graphene. The structural modification upon adsorption of each molecule on a monolayer of graphene was extracted, and
the essential features are listed in table 1 (further information in table S1 (available online at stacks.iop.org/JPMATER/3/034011/mmedia)).

The interaction distance ($d_{avg}$, in Å) is reported as the average distance between the planes of the iminotriazine rings and graphene. In all cases, the observed distances are in the range of 3.3–3.4 Å, which are typical distances observed with other aromatic molecules on carbon nanostructures [51]. The dihedral measurements are consistent with the almost complete planarity of the adsorbed molecules (figure 1(a)). As for the structural integrity of graphene, the root mean square deviation (RMSD in Å) was calculated for graphene before and after adsorption. This deviation is minimal, and graphene must, therefore, suffer very little structural deformation.

In order to account for the electronic properties of these systems, the binding energies ($E_{ads-ITx}$) between ITx and graphene were calculated using the following equation,

$$E_{ads-ITx} = E_{G-ITx} - (n \cdot E_G) - (m \cdot E_{ITx})$$  \hspace{1cm} (1)

where $E_{G,ITx}$, $E_G$, and $E_{ITx}$ are the total energies of the total systems, the isolated graphene and the isolated iminotriazine molecule, respectively. The n and m indexes are the number of graphene unit cells in the total system and the number of adsorbed iminotriazine molecules, respectively. The total adsorption energies have been decomposed further in three main contributions:

$$E_{ads-ITx} = E_{G-ITx} + E_{G-dis} + E_{ITxsupra} =$$

$$E_{ads-ITx} = (E_{G-ITx} - E_{G\prime\prime} - E_{ITxsupra}) + (E_{G\prime\prime} - n \cdot E_G) + (E_{ITxsupra} - m \cdot E_{ITx})$$  \hspace{1cm} (2)

where $E_{G\prime\prime}$ and $E_{ITxsupra}$ are the total energies of the graphene layer and the imino triazine assembly, respectively, taken from the G-ITx total system equilibrium structure. From this analysis, we can determine the direct interaction energy between the imino triazine derivative and graphene ($E_{G-ITx}$), the distortion energy of graphene from its unperturbed equilibrium structure ($E_{G-dis}$) and the cohesive energy of the iminotriazine supra-molecular network ($E_{ITxsupra}$). For estimating the prevalence of the π-π interaction or the dispersion forces, we extracted the adsorption energy without the consideration of the dispersion forces ($E_{ads-no-dis}$) from the optimised structures as implemented in our calculations:

$$E_{ads-ITx} = E_{ads-no-dis} + E_{disp}.$$  \hspace{1cm} (3)

The binding energies and their decompositions are collected in table 2.

Based on these results on the $E_{ads-no-dis}$, we can determine that, at least in the case of iminotriazine with graphene, the main contribution to the interaction are the dispersion forces, not the π–π interactions. In the cases of these iminotriazines, the dispersion forces account for 66% (on average) of the interaction forces between the ITx molecules and the graphene layer. The term for the direct interaction between the IT1, IT3 and IT4 molecules and graphene ($E_{G-ITx}$) indicate that all iminotriazines have the same level of interaction with graphene (within 0.1 eV). In IT2 the p-amino groups produce a stronger interaction with the graphene, a fact that has been reported previously in the literature [24]. The interaction between the molecule and graphene produces a small distortion in the graphene planarity. This distortion energy ($E_{G-dis}$) is significant (around 0.5 eV). This distortion is constant for all of the different iminotriazines, which is consistent with the RMSD values obtained for the graphene monolayer. The overall interaction is comparable to those of other polycyclic aromatic molecules adsorbed on graphene [52].
Table 3. Non-covalent interaction of ITx with graphene in DMF.

| Sample       | mmol ITx/mg graphene |
|--------------|-----------------------|
| IT1 + FLG    | 1.69E–06              |
| IT2 + FLG    | 5.61E–06              |
| IT3 + FLG    | 6.94E–06              |
| IT4 + FLG    | 3.45E–06              |

Calculated by thermogravimetric analysis at 580 °C.

Previous studies in our group, have shown that the formation of a supramolecular network produces an additional stabilisation due to the intermolecular interactions between molecules (measured by $E_{ITxsupr}$) [49]. The supramolecular interaction between a horizontal sheet formed by iminotriazines and graphene was also studied, with iminotriazine IT1 selected as a model (table S2 and figure S1). Different possible bonds between iminotriazine molecules (head-head, head-side and side-side) were investigated, and it was concluded that the interaction that governs the formation of the sheet is side-side, with two stabilising hydrogen bonds between the NH$_2$ group and triazine nitrogen, as well as an interaction between an ortho-phenyl proton and a triazine ring nitrogen. We observed that the supramolecular contribution ($E_{ITxsupr} = −0.7$ eV) of IT1 is much more modest than the direct electronic interaction ($E_{D−ITx} = −2.5$ eV) (table S2). We concluded that the formation of a supramolecular network is not as favourable as in previous cases [49]. The low tendency to form these networks could account for the inability of these molecules to exfoliate graphite.

2.2. Experimental interaction of graphene with iminotriazines

The interaction of graphene with the iminotriazines was studied in order to corroborate the theoretical predictions on the modification of the electronic properties of graphene [25, 53]. Few-layer graphene (FLG) dispersions were prepared using a mechanochemical treatment previously reported by us [25, 54] and described in the experimental section (4.1.5). 20 ml of a dispersion of FLG (0.2 mg ml$^{-1}$) in DMF were mixed with the iminotriazines (IT1–IT4) for 24 h. After this time, the sample was centrifuged to precipitate the graphene material, and the supernatant solution was removed to eliminate the excess of iminotriazine in solution. Finally, the solids were redispersed in fresh DMF for further characterisation, as mentioned in the experimental section (4.1.6).

Thermogravimetric analysis (TGA) provided insights into the composition of the material in dispersion after the interaction process (table 3). Samples of FLG with iminotriazines IT1–IT4 showed weight losses starting at around 300 °C, which corresponds to the organic compounds. This weight loss had stabilised at 580 °C, and this information was used to calculate the amount of iminotriazine derivative in each ITx + FLG sample (figure S3 in supporting information).

These results correlate nicely with the theoretical results and the relatively small adsorption energies of these molecules. Dispersions were also characterised by Raman spectroscopy. This technique is a versatile tool for studying the structural and electronic properties of graphene [55]. In particular, this technique helps to discriminate between graphite and few-layer graphene [55]. In our case, the main peaks of graphene (D-, G- and 2D-bands) were monitored to probe disorder or rationalise the non-covalent interactions of the iminotriazine molecules through defect-activated graphene peaks [56]. The modifications of the Raman bands after interaction of iminotriazines and graphene are collected in table S3.

Comparison of the positions and intensities of the D-, G- and 2D-bands of FLG and ITx + FLG samples shows that the non-covalent interactions do not significantly modify the electronic properties of FLG (table S3). To justify these variations, the ratios of the intensities $I_D/I_G$ and $I_{2D}/I_G$ were determined, and only small variations were observed in $I_D/I_G$ between the samples. In this case, it can be stated that there was a small increase in the number of defects on FLG when the iminotriazine was absorbed non-covalently [57]. The variation in the position of the D and 2D bands has been used in the literature to identify n- or p-doping due to interactions of the absorbed molecules with the graphene layers [58]. In our case, the Raman spectra of the IT3 + FLG sample are shown in figure 2, and it can be seen that there is only a small variation in the positions of the D- and G-bands with respect to the FLG sample. The variation in the position of the 2D band is between $−1.57$ and $−4.09$ cm$^{-1}$ for the ITx + FLG samples, which is consistent with n-doping (figures S4(a)–S7(a), table S3) in literature [58].

It is known that graphene can produce a reduction or complete quenching of the fluorescence of several substrates due to the charge transfer effect from the parent compound to graphene [59]. The absorption and emission spectra of IT3 and the IT3 + FLG sample are shown in figures 3 and 4.

It can be seen from the absorption spectra in figure 3 that there was an increase in the intensity and a bathochromic shift of the band at 325 nm while the emission spectra (figure 4) show a marked reduction in
the emission intensity. Both effects confirm that an effective interaction between IT3 and FLG occurs through π-π-interactions. Similar results were obtained in the UV–vis and fluorescence spectra of the other iminotriazines and ITx + FLG samples (figures S4(b)–7(b)).

The modification of the electronic properties of these ITx molecules on graphene was also analysed. This analysis was carried out by calculating the Projected Density of States (PDOS) on the relaxed structure, where modification of the bandgap of graphene could indicate variations in its electronic structure (figure 5). The electronic density of graphene (figure 5(a), dark green) remains unchanged when compared to the pristine graphene (figure 5(a), FLG). These theoretical results led us to conclude that the adsorption of the iminotriazine does not affect the zero-band gap of graphene. There is no charge transfer effect between the graphene and the iminotriazines since the typical V-shape of graphene at the Fermi level remains unchanged.
Figure 5. (a) PDOS at PBE level for the ITx/graphene systems. Colour code: carbon graphene (green), carbon ITx (black), nitrogen (light blue), oxygen (red), sulfur (orange). For visualization purposes, the contributions from the s orbitals have been omitted. (b) Perspective view of the IT1–IT4 molecules on graphene. Colour code: carbon graphene (light green), carbon ITx (dark green), nitrogen (light blue), oxygen (red), sulfur (yellow) and hydrogen (light pink).

Table 4. Computed bandgap (Eg) and dipolar moment variation (Δµ) and experimental bandgap (Exp. ΔEg) upon adsorption of IT1–IT4 derivatives on graphene.

| Entry | ΔEg (eV) | Δµ (D) | Exp. ΔEg (eV) |
|-------|----------|--------|---------------|
| IT1   | −0.03    | −0.03  | −0.31         |
| IT2   | −0.21    | −1.29  | −0.03         |
| IT3   | −0.18    | −2.12  | −0.06         |
| IT4   | −0.03    | 0.01   | −0.07         |

However, we observed a small experimental variation on the ITx-FLG Raman spectra. There are examples in the literature where a small charge transfer (0.18e) correlates with experimental variations on their Raman spectra (around 5 cm\(^{-1}\)) [60]. We could not identify such small charge transfers in our case, as it could be that it is too low to be measurable based on the PDOS analysis. We also considered possible to observe this weak interaction with the slight variations in the molecular PDOS levels of the adsorbed ITx molecules (ΔEg) when compared with the PDOS levels of the isolated molecules (figure S2). The term Δµ corresponds to the dipolar variation upon adsorption, and Exp. ΔEg corresponds to the experimental variation bandgap. The results for the band gaps and dipole moments before and after adsorption are collected in table 4.

The comparison of the experimental optoelectronic properties and the closely related theoretical results shows in both cases very small variations of bandgap and dipolar moment values (table S4). These results do not present a clear trend between the experiment and the in-silico results, mostly due to the small interaction and small quantities of molecules absorbed on graphene. Also, the small variations found in the experimental results are below the computational error of the theoretical method used in this study.

3. Conclusions

In conclusion, we have studied the interaction of these iminotriazines with graphene both theoretically and experimentally. We have concluded that the main contribution on the adsorption energies between the ITx and graphene are the van der Waals forces. The average contribution of dispersion term to the overall adsorption energy (avg. 66%). These theoretical results are also in good correlation with the experimental results, given the small quantity of iminotriazine molecules adsorbed on graphene.

The optoelectronic properties of the organic molecules and the nanomaterials were also studied both theoretically and experimentally by the variation of the Raman properties, UV–vis and fluorescence spectra. Experimentally, we observed small variations of the optoelectronic properties, which could also be linked to the small quantity of adsorbed molecules. On the theoretical results, we observed that the structure of graphene is not affected upon adsorption; hence this sort of molecules could be potentially used to combine with our nanomaterials without loss of its inherent properties. In the cases of IT2 and IT3, the theoretical bandgap change was around 0.2 eV, possibly because of variations in the dipole moments upon adsorption. However, we could not observe a specific trend of the theoretical results with these molecules, mainly because of the small variation of the experimental results is below the accuracy of the computational method used for this study. However, this work could help to understand better the nature of the interactions between iminotriazines and graphene and contribute to the design of new strategies to modify the optoelectronic properties of graphene.
4. Experimental

Solvents were purchased from SDS and Fluka. Chemicals were purchased from Sigma-Aldrich and used as received. Graphite was purchased from Bay Carbon, Inc. (SP-1 graphite powder, www.baycarbon.com) and used without purification. Iminotriazines IT1–IT4 were synthesised by a previously reported protocol [61].

4.1. Experimental details

4.1.1. Raman spectroscopy

Raman spectra were recorded on an InVia Renishaw microspectrophotometer equipped with a 532 nm point-based laser. In all cases, power density was kept below 1 mW µm−2 to avoid laser heating effects. Raman samples were measured in the solid-state under ambient conditions. The resulting spectra (after at least 30–40 random locations on each sample) were fitted with Lorentzian-shaped bands in their D, G and 2D peaks to ascertain band positions, widths and intensities.

4.1.2. UV spectroscopy

UV–Vis-NIR spectra were recorded in a 1 cm quartz cuvette on a Cary 5000 spectrophotometer.

4.1.3. Thermogravimetric analysis (TGA). Thermogravimetric analyses (TGA) were performed with a TGA Q50 (TA Instruments) at 10 °C min−1 under a nitrogen flow from 100 °C to 800 °C. Samples were prepared by filtration of the final dispersions through a membrane filter (Millipore GTTP of 0.2 µm).

4.1.4. Fluorescence spectroscopy

Fluorescence spectra were recorded with a Photon Technology International, Inc. spectrofluorometer with a slit width of 1 nm and quartz cuvettes with a 10 mm path length. The fluorescence spectra of ITx and ITx + FLG were measured using the same concentration of ITx. The quantity of ITx on each sample of ITx + FLG was calculated by TGA.

4.1.5. Synthesis of FLG

Graphene dispersions in DMF were prepared using a ball milling method with graphite and melamine as the exfoliating agent [25]. In a typical experiment, 7.5 mg of graphite and 22.5 mg of melamine were placed in a 25-ml steel jar with ten stainless steel balls of 1-cm diameter. The jar was inserted into the planetary ball-milling machine (Retsch pm100) for 30 min at 100 rpm. After the milling treatment, the resulting product was dispersed in 20 ml of DMF. Concentrated dispersions of graphene/melamine in DMF were washed by filtration to remove melamine.

4.1.6. Preparation of FLG–IT1–4 dispersions

20 ml of FLG dispersion in DMF (0.2 mg mL−1) and iminotriazine derivatives IT1–IT4 (0.03 mmol) were sonicated for 1 min in a round-bottomed flask. The solutions were stirred for 24 h under ambient conditions. After the treatment, two aliquots of 10 ml of the dispersions were centrifuged at 1200 rpm for 10 min. After being centrifuged, both solids were redispersed in 10 ml of fresh DMF and analysed by Raman, UV and fluorescence techniques, and the other 10 ml were filtered prior to analysis by TGA.

4.2. Computational details

The structural and electronic features of IT1–IT4 molecules on graphene were characterised by periodic spin-polarised density functional theory (DFT) [62, 63] with the standard projector augmented wave (PAW) potentials [64, 65], as implemented in the VASP code [66–68]. The Perdew–Burke–Ernzerhof (PBE) [69, 70] functional with a kinetic energy cut-off of 750 eV was used to converge the plane-wave basis set for all calculations. The supramolecular networks were relaxed using the conjugate gradient method until the forces were below 0.03 eV/Å on all atoms. Each graphene cell was modelled with a vacuum space larger than 15 Å between repeated images and corrected dipole correction in the vacuum gap [71].

The dispersion-corrected DFT scheme (DFT-D) proposed by Grimme [44] was employed, where weak interactions are accounted for as a general dispersion correction to the DFT energy given by an attractive semi-empirical pair potential. This methodology is being extensively used in the literature for carbon-based nanostructures [72–74] and delivers results that are qualitatively comparable to those obtained by more expensive computational methods with experimental data. In particular, the most recent DFT-D, i.e. DFT-D3, was used with the Becke–Johnson damping function (BJ) [45, 46], as implemented in VASP. A Γ–center 21 × 21 × 1 k-point mesh grid was used for the graphene unit cell, and different divisions were used in each case depending on the size of the cell under study. The Brillouin zone was integrated with the
Gaussian smearing method (0.01 eV as smearing width), except in the case of the density of state analysis (PDOS), where a tetrahedral smearing method was used. Dipole moments were obtained using the Gaussian 09 code\cite{26} at the DFT-PBE(D3BJ)/6-311 + + G(2d,2p) level of theory on the periodic VASP-PBE minimum energy geometry.

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Conflicts of interest

‘There are no conflicts to declare.’

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