# Electronic Properties of Adsorption of Trimesic Acid Monomer on Graphene

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**Abstract.** A large scale approach based on scanning tunneling microscopy $STM$ simulation images and *ab initio* computation is used to report the adsorbed trimesic acids ($TMA$) monomer and monolayer behaviors on graphene. Our results unravel the interplay between the adsorption energy and band gap opening for different adsorption sites of TMA/graphene. It has been revealed that regarding to stability of different adsorption site and interaction with $\pi$ electron containing surfaces (graphene), the high adsorption energy can induce maximum band gap in the system and open up possible uses of graphene in electronic device applications. A vital role on carboxyl functional groups is related to duality behaviors of combined acceptor and donor character with regard to hydrogen bonds which provides stable intermolecular self-assembly[1] and monolayers (for detailed explanation and analysis see reference [1]).

## 1. Introduction
A holistic understanding of the molecular self-assembly as one of the most ubiquitous driving forces in materials design in natural world,[2,3,4] engineering complex porous organic nanoarchitectures[5,6,7,8,9] is the focus of recent research interest and paramount importance. Nature molecular self-assembly such as spider silk,[10] DNA[11] and cellular membranes[12] demonstrate the potential for encoding information[2] and for producing biological function as well as permanent nanoporosity[13] can be exploited after subsequent functionaization for developing novel nanostructured materials dedicated to catalysis, gas storage, selective ion exchange, high density data storage[4] using only a small number of relatively simple molecular building blocks. Molecular self-assembly as key point which offers unique directions for the fabrication of two-dimensional organic nanoarchitectures.[5]

Moreover, carboxylic functional can significantly alter $\pi - \pi$ interactions between graphene surface and the adsorbed molecules. In the present study, we have focused on this functional group for the adsorption of trimesic acid on the high symmetry sites of graphene with using first-principals calculations based on the density functional theory (DFT). To understand the adsorption better, we compare the properties of TMA/graphene with the pristine graphene. The stability, electronic structure and adsorption profile of this molecule with different configurations were analyzed in detail. We found that the TMA/graphene can induce a gap on graphene. With the local analysis of STM simulation images and local density of states (charge accumulation) and charge transfer mechanism, we can clarify the origin of band gap opening in the system.
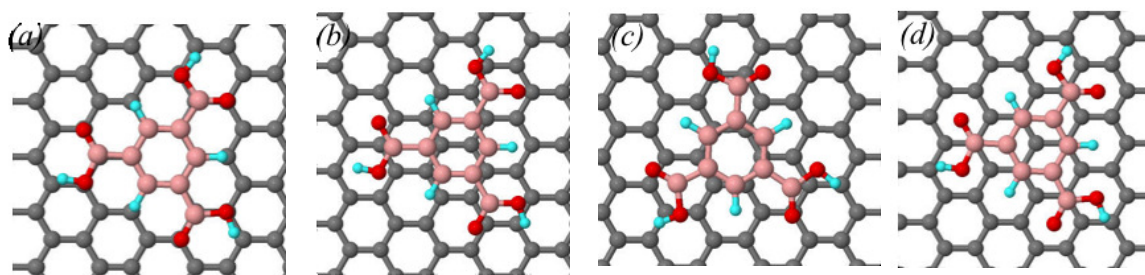
**Figure 1.** *High symmetry configurations, (a) top, (b) bridge, (c) cross and (d) center. For clarity, we chose pink for the carbon atoms, cyan for hydorogen atoms and red for oxygen atoms of TMA.*

## 2. Results and discussions

*2.0.1. Stability and adsorption configuration* Carboxylic groups (COOH) for intermolecular hydrogen bonding are very interesting functional units that has been used extensively to engineer crystals in 2D and 3D.[14] Rochefort and his co-workers studied effect of substituents and their interactions by comparing the adsorption of benzene, benzoic acid (1=BZA), isophthalic (2=IPA) and trimesic acid (3=TMA) on graphene.[14] However, in order to gain a more fundamental understanding and reliable predictions of the adsorption properties of the aromatic molecules like as trimesic acid (TMA) which can form more complex configuration on the graphene plane, in this feature article, we will begin and describe our theoretical analysis by comparing the adsorption of TMA on various high symmetry sites on graphene. Several positions of the TMA molecule relative to graphene sheet were considered near four symmetry sites on graphene, such as *top, bridge, cross* and *center* as can be seen in figure 1.

The first site is labeled as *top* which follows the atomic species sitting on top of the carbon atom in graphene. The other three sites are labeled as *bridge*, which means one $C - C$ bond of graphene is under the center of the TMA molecule and *cross*, which means all molecular atoms are located at top of middle of $C - C$ bond and the last one, *center* means that the one carbon atom is placed at the center of benzene ring in TMA molecule.

Our systematic study begins with the structural optimization results for adsorption of single TMA molecule on described high symmetry sites of graphene. A summary of the acquired results such as adsorption energy, equilibrium central core distance, band gap energy and net charge for different TMA adsorption sites is presented in Table 1. As shown in the Table, these different sites have significantly effect on adsorption process and electronic properties.

Further analysis of Table 1 can be performed to identify the following common trend features: (1) *top* and *cross* are the most stable adsorption sites for TMA molecule and *center* and *bridge* sites are the less stable configuration respectively, (2) the equilibrium vertical distance of aromatic ring on *top* and *cross* site is larger than *center* and *bridge*, (3) the minimum band gap is found at the *bridge* site which is 17 meV, whereas the maximum band gap is found at top site which is 48 meV, (4) *bridge* configuration shows maximal net charge transferring from graphene to TMA which amount is found -0.18$e$, so that charge transfer ordering for other site is arranged as center, *cross* and *top* configuration, also with increasing the adsorption energy, the charge transfer is decreased as well as band gap opening is increased.
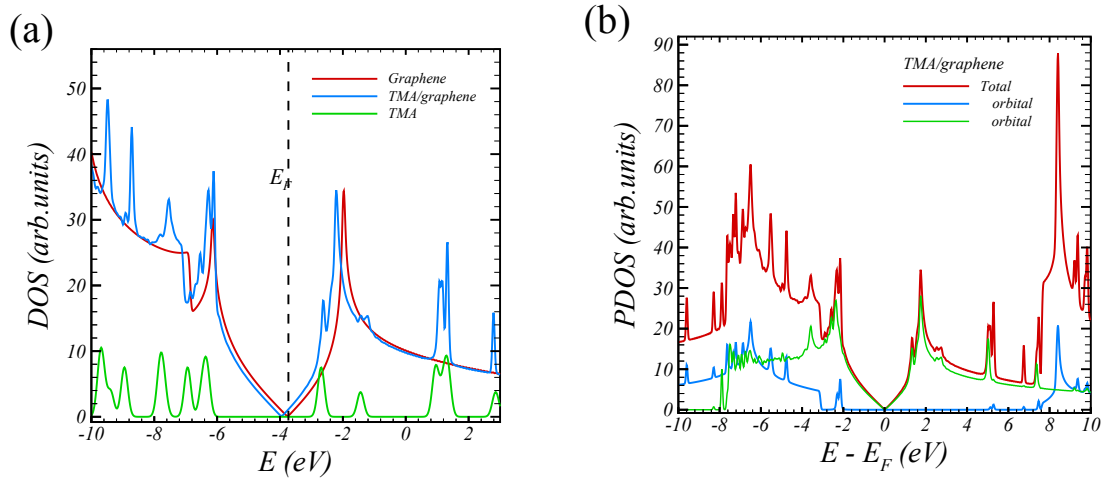
**Figure 2.** *(a): Density of state (DOS) of isolated graphene sheet, TMA adsorption on graphene (bridge site) and isolated trimesic acid (TMA). The Fermi-energy shifts around of 0.1 eV for bridge site, (b): projected density of state of total atoms for TMA/graphene.*

TABLE 1. *Adsorption energy,band gaps energy, equilibrium distance and net charge transfer of isolated graphene with all sites of TMA/graphene, $\Delta Q = Q_{TMA/Ge} - Q_{Ge}$.*

|  | **Top** | **Bridge** | **Cross** | **Center** |
|---|---|---|---|---|
| $E_{\text{ads}}$ (eV) | -2.22 | -1.25 | -2.13 | -1.83 |
| $\Delta E_g$ (meV) | 48 | 17 | 47 | 19 |
| $d$ (Å) | 3.08 | 2.86 | 3.06 | 2.95 |
| net charge ($|e|$) | -0.11 | -0.18 | -0.14 | -0.17 |

Via carefully analyzing the band structure of all configurations of TMA adsorption on graphene which tabulated in Table 1, we infer that the TMA molecule can open a gap according to the adsorption site. The two more stable configuration i.e. *top* and *cross* adsorption site of TMA induces the larger band gap. We ascribe these behaviors to the effect of charge transfer and induced electric field between surface and adsorbed molecule, which will be discussed next. Other than that, analyzing of Mulliken charges for deep understanding of charge transfer mechanism, with defining of $\Delta Q = Q_{TMA/Ge} - Q_{Ge}$ as net charge, has been acquired and presented in Table 1. The net charge transfer from graphene to TMA changes for different configuration, the more stable adsorption sites show less charge transfer than the weaker adsorption sites. TMA molecule on *top* and *cross* receive $0.11e$ and $0.14e$, whereas charge transfer for *center* and *bridge* is $0.17e$ and $0.18e$, respectively. The measured distance of carbon atoms of graphene and oxygen atoms of $C = O$ of TMA (as mentioned previously) clearly illustrate the competing role of this distance on maximizing the charge transfer. For instance, minimum distance for *bridge* results maximum charge transfer.

*2.0.2. Electronic properties*   Here we give results for the electronic structure of TMA/graphene. Figure 2 shows the total electronic density of states (DOS) for pristine graphene as a reference, isolated TMA and bridge adsorption site of TMA/graphene studied here.   As clearly seen, the density of states (DOS) of TMA/graphene isn't be significantly changed, (DOS(TMA/graphene)≈DOS(*graphene*) + *DOS(TMA)*) only the states of graphene are somehow perturbed due to adsorption of TMA, i.e. the adsorption of TMA on graphene
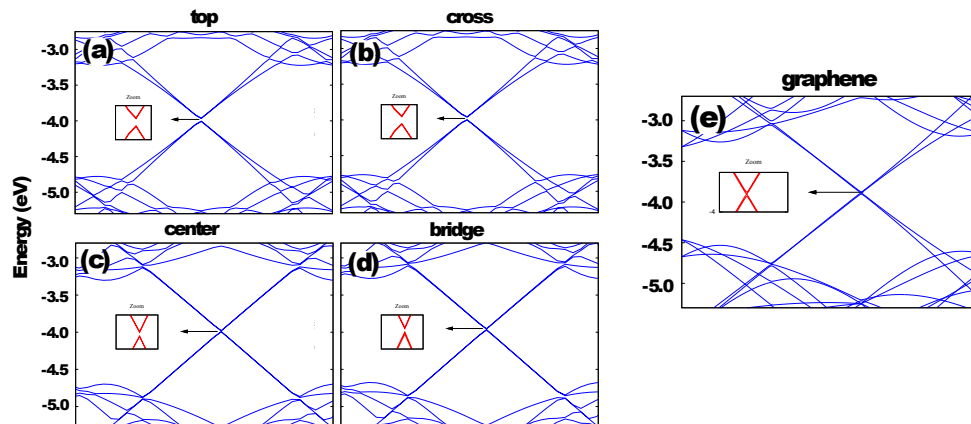
**Figure 3.** *Band structure of pristine graphene and TMA/graphene in isolated graphene and four different adsorption configurations. The insert provide more detailed band structures near the fermi level. The linear band property of $\pi$ orbital is maintained.*

is relatively weak but due to the existence of three $COOH$ carboxylic acids level, (electron-withdrawing character of the $C = O$ in carboxyl functional groups) the electrons were moved from the valence bond of graphene to TMA molecule thereby this adsorption slightly shifts $0.1eV$ Fermi-energy into the valence band. It's worth mentioning that the shifting in Fermi energy level indicates $p$ doping, confirms charge transferring between the molecule and graphene.

To investigate the $\pi - \pi$ interaction between the graphene and TMA, figure 2 (right panel) presents the variation of the projected density of states of $\pi$ and $\sigma$ orbitals of total atoms for TMA/graphene. The presented results in right panel of figure 2 suggest that $\pi$ orbitals contribution dominated the DOS in the vicinity of Fermi energy.

In order to study the effect of molecule adsorption on the electronic properties of graphene, the band structure of four adsorption configurations of TMA on graphene as well as pure graphene are plotted and analyzed in figure 3. It's been clearly seen that the band structure of the TMA/graphene system is very similar to pure graphene. Thus the interaction between TMA and graphene is weak, near the Dirac point of two $p_z$ bands, linear dispersion still exist. With providing zoom in the region near the Dirac point as the inset in figure 3, we discover the *top* and *cross* configuration induced the band gap larger than *center* and *bridge* site (Table 1, figure 6). This band gap opening can be attributed to electric field vertical to the graphene due to the molecule-graphene charge transfer, which breaks the inversion symmetry of graphene (see reference [1] ).[1]

Figure 4 gives the influence of different adsorption sites of TMA/graphene on STM contrast simulation. In upper panel of figure 4, we plotted the topographic STM simulation images of different sites defined in figure 1. STM images shows a remarkable atomic resolution of the surface. An extended analysis of STM contrast along two horizontal black line directions A (neighbor of TMA) and B (underneath of TMA) is performed in figure 4(middle panel) which the position of molecule and graphene is reversed. The existed periodicity between maxima and minima along line A and B for isolated graphene have a little bit difference. However, the periodicity for graphene of neighbor and underneath of TMA molecule zone, i.e. 8-16 $\mathring{A}$ modifies to weak peaks and includes significant deformations over different sites adsorption. In middle panel of figure 4, 2D profile (maxima and minima peak) at line A displays $C - C$ bond corrugation related to neighbor of TMA molecule for all sites placed with larger amplitude from B line profile, moreover this separation for bridge and center sites is more pronounced
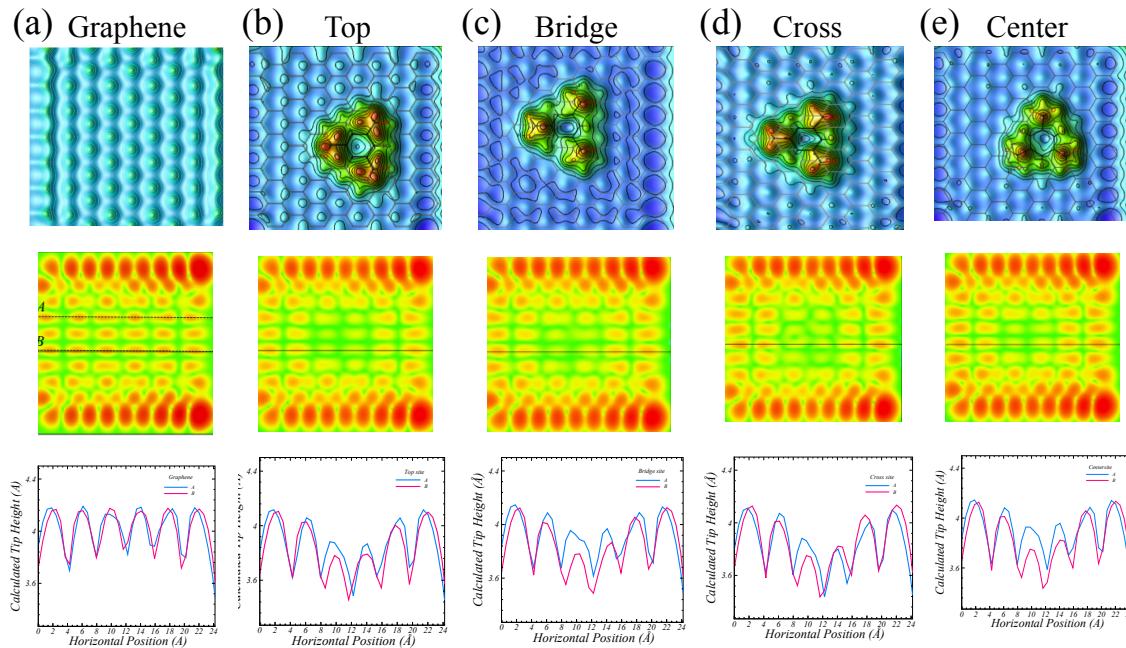
**Figure 4.** *Top panel: STM simulation images for different site adsorption of TMA molecule on graphene; left to right organized as top, bridge, cross and center sites as depicted in figure 1, middle panel: analysis of 2D simulation profiles; last panel: variation of tip distance for black horizontal A and B line, lower panel: particular of the middle panels with definition of differential tip hight, $\Delta h = h_A - h_B$.*

in comparison with two other sites. As a consequence, surface deformation in neighbor region of TMA for top and cross is more intense related to bridge and center sites. In other words, large perturbation term over two more stable, i.e. cross and top adsorption sites exists in TB-hamiltonian which breaks the symmetry of surface for neighboring effect and result in decreasing of degeneracy degrees or enhanced band gap opening over these two sites relative to instable sites.

## 3. Conclusions

The effects of adsorbing trimesic acid molecule on the electronic structure of graphene were systematically examined by first principle calculations. Different adsorption sites related to the position of central mass of TMA regard to graphene, affects electronic properties of system such as adsorption energy, band structure and charge transfer. We found that molecular adsorption TMA/graphene lead to band gap opening, while the magnitude of band gap depends on the adsorption site. This trend was acquired: the most stable configuration of molecule lead to the biggest band gap opening. We further analyzed the charge transfer mechanism for different adsorption sites and discovered that they play a significantly role in controlling the band gap. The intrinsic lateral charge transport characteristics has been affected by geometry of TMA adsorption on graphene.

## 4. Acknowledgments

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