

# Supplementary Materials for “Optical and electronic properties of graphene nanoribbons upon adsorption of ligand-protected aluminum clusters”

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## I. BADER CHARGE ANALYSIS

We performed Bader charge analysis on the systems where the adsorbate is deposited on the center of the armchair-edge ribbon. This analysis is meant to support the Mulliken population treatment described in the article. Bader charges were obtained by post-processing the charge density data generated by SIESTA with the program written by Arnaldsson et al.[1] which computes the total charge associated with each atom. An energy cutoff of 300 Ry and SZ basis set of SIESTA[2] were used in the charge density calculations. The charge transfer values extracted via Bader analysis are: (i) -1.00 e, (ii) -0.30 e, (iii) -1.07 e and (iv) -0.17 e. These results are in accordance with those obtained via Mulliken population depicted on table 1 in the manuscript.

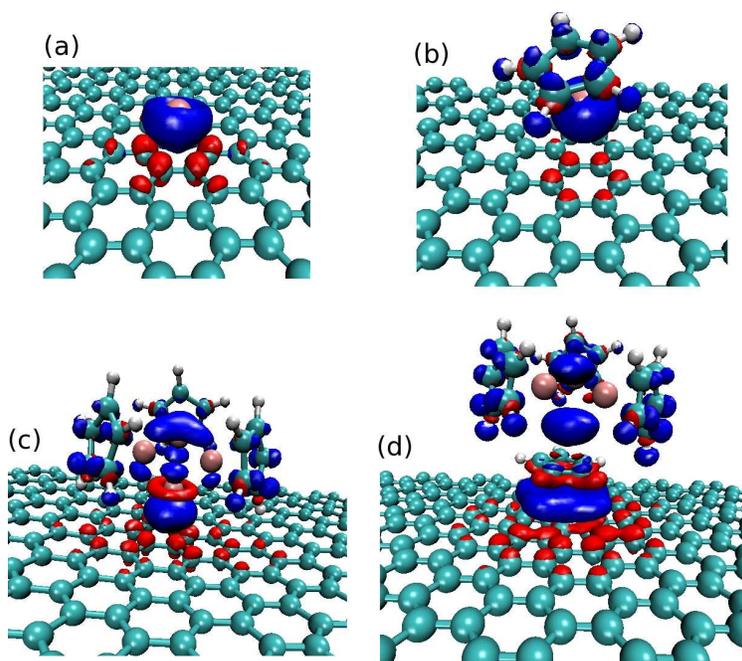


FIG. 1: (Color online) Difference in charge density after the adsorption of (a) Al, (b) AlCp, (c)  $\text{Al}_4\text{Cp}_3$ , and (d)  $\text{Al}_4\text{Cp}_4$  on the 18-AGNR. Blue and red isosurfaces represent charge depletion and accumulation, respectively. The used isosurface values are: (a,c)  $0.002 \text{ e}/\text{\AA}^3$ , (b)  $0.001 \text{ e}/\text{\AA}^3$ , and (d)  $0.00025 \text{ e}/\text{\AA}^3$ . The plots were done by using VMD visualization tool[3].

The same parameters mentioned above were adopted to calculate the difference in charge density for all center adsorption events. The charge density difference is given by  $\Delta\rho = \rho_{cr} - \rho_c - \rho_r$ , where  $\rho_{cr}$  is the electronic density of the interacting system (cluster+ribbon) and

$\rho_c$  ( $\rho_r$ ) is the density of the isolated cluster (ribbon) obtained from former relaxed positions extracted from the interacting system. The results for center adsorption are shown in figure 1. Blue and red isosurfaces represent depletion and accumulation of charge, respectively. The Al and Al<sub>4</sub>Cp<sub>3</sub> adsorptions impart a significant transfer of charge to ribbon resulting in a pronounced charge accumulation on the ribbon. Although the remaining two adsorption cases (AlCp and Al<sub>4</sub>Cp<sub>4</sub>) do not render strong charge transfer values, one can see from the figure that the interaction with the ribbon is enough to provoke a significant charge rearrangement in the cluster.

## II. ALUMINUM CLUSTER WITH PERMETHYLATED LIGANDS

In order to understand in detail the role played by the ligands in the adsorption, one extra Aluminum-based cluster system with permethylated ligands, Al<sub>4</sub>Cp<sub>4</sub><sup>\*</sup> (Cp<sup>\*</sup>=C<sub>10</sub>H<sub>15</sub>), is deposited on the 18-AGNR. These calculations were conducted using the same DFT criteria as those set for the original cluster Al<sub>4</sub>Cp<sub>4</sub> (Cp=C<sub>5</sub>H<sub>5</sub>). This cluster interacts stronger with the AGNR in comparison to the Al<sub>4</sub>Cp<sub>4</sub>; we have obtained a binding energy of  $E_b = 0.84$  eV and charge transfer of -0.4e (Mulliken population). The cluster-host average distance is  $d = 3.14$  Å and the standard deviation associated to the average z-coordinates of the host atoms is  $\sigma_z = 0.16$  Å. The way this cluster perturbs the electronic structure and optical response of the ribbon is presented on figure 2. The relaxed structure and charge density difference map are depicted in figure 3.

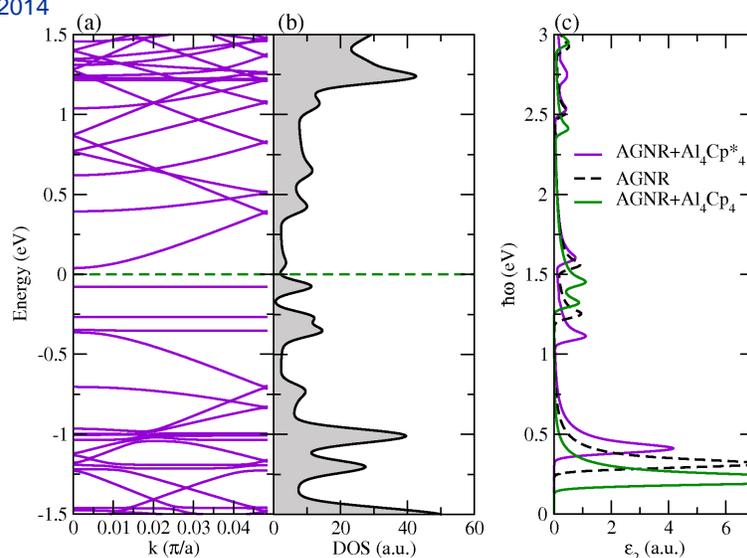


FIG. 2: (Color online) (a) Band structures, (b) Density of states (DOS) and (c) Imaginary part of the dielectric function ( $\epsilon_2$ ) obtained for the 18-AGNR upon center adsorption of the cluster  $\text{Al}_4\text{Cp}_4^*$  ( $\text{Cp}^*=\text{C}_{10}\text{H}_{15}$ ). The Fermi energy is set at 0 eV and it is marked by dashed lines. The  $k$ -vector interval spanned in the band structure is  $[0, \pi/a]$  with  $a$  the longitudinal length of the supercell. The incident light wave with energy  $\hbar\omega$  is assumed to be polarized parallel to the longitudinal direction of the 18-AGNR. Optical spectra for the isolated AGNR and upon center adsorption of  $\text{Al}_4\text{Cp}_4$  ( $\text{Cp}=\text{C}_5\text{H}_5$ ) were included on panel (c) for comparison.

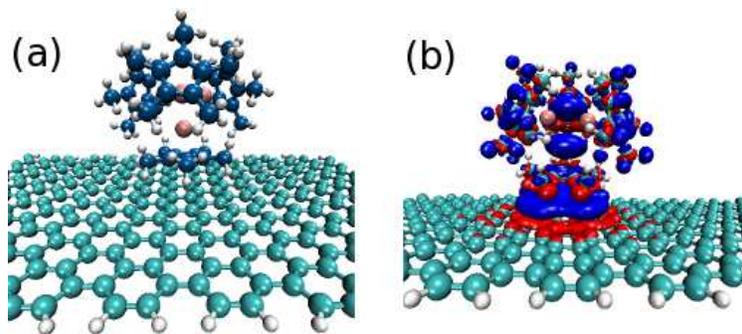


FIG. 3: (Color online) (a) Lowest energy atomic structure and (b) difference in charge density after the center adsorption of  $\text{Al}_4\text{Cp}_4^*$  ( $\text{Cp}^*=\text{C}_{10}\text{H}_{15}$ ) on the 18-AGNR. Blue and red isosurfaces represent charge depletion and accumulation, respectively. The used isosurface is  $0.0003 \text{ e}/\text{\AA}^3$ . The plots were done by using VMD visualization tool[3]. On panel (a), the carbon atoms of the ribbon and the cluster are differentiated by distinct tones of blue for better visualization.

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- [3] W. Humphrey, A. Dalke, and K. Schulten, *J. Molec. Graphics* 14.1, 33-38 (1996).