

Supporting Information

Selectivity of a Graphene Nanoribbon-Based Trinitrotoluene Detector: A Computational Assessment

Dana Krepel^{1,*}, Oded Hod^{1,2,†}

¹*Department of Physical Chemistry, School of Chemistry, The Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 6997801, Israel*

²*The Sackler Center for Computational Molecular and Materials Science, Tel Aviv University, Tel Aviv 6997801, Israel*

**Present address: Center of Theoretical Biological Physics, Rice University, Houston, Texas, 77030*

†Corresponding author: odedhod@tau.ac.il

Assessment of the Effects of Dispersion Correction

The systems considered in the present study consist of pristine zigzag graphene nanoribbons (ZGNR) decorated with lithium adatoms that serve as anchoring sites for the chemisorption of contaminant molecules. This strong surface binding mechanism suggests that the screened-hybrid HSE¹⁻⁴ exchange-correlation density functional approximation used herein should provide a good description of the structural and electronic properties of the studied systems even without the inclusion of long-range dispersion effects. To assess the validity of this assumption we performed comparative calculations of the optimal structures and spin-resolved bandgaps of the toluene and TNT adsorbed (8x12) ZGNR obtained with and without the inclusion of dispersion corrections.

To describe long-range dispersion effects we adopted Grimme's D3 dispersion correction scheme^{5,6} as implemented in the Gaussian suite of programs.⁷ Due to some technical limitations of the D3 implementation within the version of the Gaussian suite of programs that we used⁷ we could not explicitly use the HSE functional or periodic boundary conditions (PBC) in these calculations. Therefore, we have adopted an alternative approach, where the armchair edges of the previously optimized (as detailed in the main text) toluene and TNT adsorbed (8x12) ZGNRs were first hydrogen passivated to form non-periodic systems. Then, their geometry was optimized using the semi-local exchange-correlation density functional of Perdew, Burke, and Ernzerhof (PBE)⁸ augmented by Grimme's D3 dispersion correction.^{5,6} The optimized lithium-contaminant complex was then placed atop the original (8x12) ZGNRs to perform single-point PBC calculations using the HSE functional.

The corresponding system coordinates can be found in the Supporting Information. Due to the relatively large unit-cell size of the (8x12) ZGNRs we expect the effect of using a finite flake during the geometry optimization stage to be of minor importance. Furthermore, the optimized geometry is expected to be only mildly affected by the fact that we use the dispersion correction in conjunction with the PBE instead of the HSE functional approximation.

Table S1 presents the distance between the lithium adatom and the atoms of the closest TNT nitro group or the basal plane of the toluene molecule (see Fig. S1) as well as the spin-resolved electronic bandgap obtained for the TNT and toluene doped (8x12) ZGNRs with and without the dispersion correction. We find that, when applying the dispersion correction, the distance between the Li adatom and the atoms of the nearby nitro group change by ~12% or less and its distance from the basal plane of the toluene molecule changes by less than 1%. Correspondingly, for the TNT adsorbed system the α bandgap changes by ~7% from 0.801 eV to 0.858 eV and the β bandgap changes by ~0.5% from 1.096 eV to 1.090 eV; while for the toluene adsorbed system the α bandgap changes by 3.5% from 0.284 eV to 0.294 eV and the β bandgap changes 6% from 0.797 eV to 0.845 eV. These variations are considerably smaller than the differences found in the main text between the bandgap of the TNT adsorbed ZGNR and that of the precursor or background molecules adsorbed systems, thus indicating that our general conclusions are insensitive to the neglect of dispersion effects.

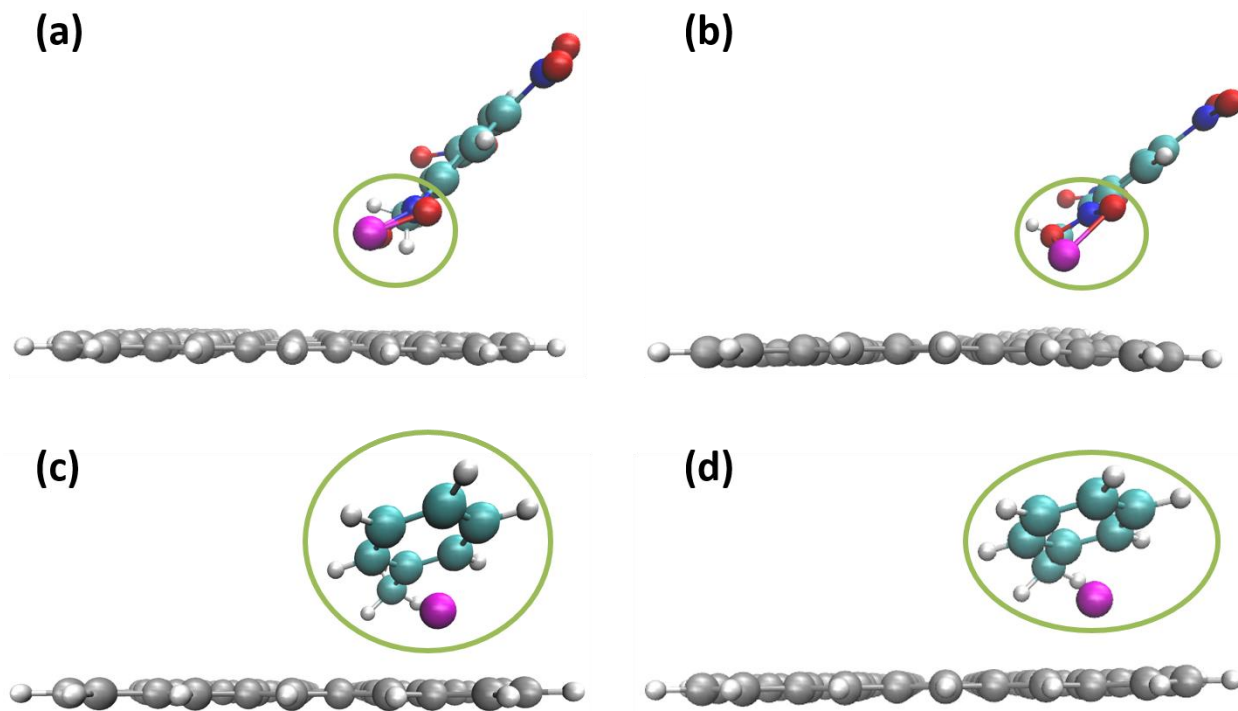


Figure S1. Schematic representation of TNT (panels (a) and (b)) and toluene (panels (c) and (d)) molecules adsorbed at a lithium anchoring site atop an (8x12) graphene quantum dot calculated with (panels (b) and (d)) and without (panels (a) and (c)) dispersion correction. For TNT adsorption, the distance between the lithium adatom and the atoms of the adjacent nitro group serve to evaluate the geometric variations upon inclusion of dispersion correction. For toluene adsorption, the average distance between the lithium adatom and the basal plane of the molecule was used for these evaluations. Both groups are marked with green circles.

Table S1. Effects of dispersion correction. Comparison of some inter-atomic distances and spin-resolved electronic bandgaps obtained for the TNT and toluene adsorbed (8x12) ZGNR as calculated before and after the inclusion of long-range dispersive interactions correction as detailed above.

		Without dispersion correction	With dispersion correction	Differences (%)
TNT	N–Li distance	1.715 Å	1.784 Å	4.0
	O ₁ –Li distance	1.386 Å	1.557 Å	12.3
	O ₂ –Li distance	1.687 Å	1.642 Å	2.7
	α bandgap	0.801 eV	0.858 eV	7.1
	β bandgap	1.096 eV	1.090 eV	0.5
Toluene	Toluene basal plane – Li distance	2.473 Å	2.458 Å	0.6
	α bandgap	0.284 eV	0.294 eV	3.5
	β bandgap	0.797 eV	0.845 eV	6.0

Ground State Spin Multiplicity Analysis

In the main text, when studying the adsorption of individual molecular contaminants on the lithium anchoring sites, we have presented results for the doublet spin configuration. To verify that this is indeed the ground spin state we have repeated the calculations for the triplet spin state. We note that for the type of systems considered herein the singlet spin state is typically higher in energy than both the doublet and triplet spin states.⁹ In table S2 we present the total energy differences between the doublet and the triplet spin state of the various TNT derivatives considered. As mentioned in the main text, for the doublet spin state the calculations involved a single lithium-molecule complex adsorbed per super-cell. The corresponding triplet state was obtained for a duplicated super-cell decorated with two laterally distant lithium-molecule complexes located on opposite sides of the ZGNR sheet. Overall, the doublet/triplet total energy differences are found to be smaller than 35 meV/super-cell mostly in favor of the doublet spin state. Therefore, we focused on the results of this spin state when discussing single contaminant adsorption per super-cell in the main text.

Table S2. Doublet/triplet total energy differences obtained for the various molecular contaminants adsorbed on the lithium decorated (8x12) ZGNR super-cell investigated in the main text.

Molecular Identity	$\Delta E_{doublet-triplet}$ [eV/super-cell]
Toluene	0.0005
o-MNT	-0.0255
p-MNT	-0.0241
2,4-DNT	-0.0348
2,6-DNT	-0.0316
TNT	-0.0177

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