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Armchair Boron Nitride nanotubes—heterocyclic molecules interactions: A computational description

Abstract: Ab-initio calculations using density functional theory (DFT) are used to investigate the non-covalent interactions between single wall armchair boron nitride nanotubes (BNNTs) with open ends and several heterocyclic molecules: thiophene (T; C_4H_4S), benzothiophene (BT; C_8H_6S) and dibenzothiophene (DBT; $C_{12}H_8S$). In the armchair model the nanotubes exhibit (n, n) chirality; here we consider n = 5. The exchange-correlation energies are treated according to the Hamprecht-Cohen-Tozer-Handy functional in the generalized gradient approximation (HCTH-GGA). A base function with double polarization is used. The geometry optimization of (5,5) BNNT-X; X = T, BT and DBT has been carried out using the minimum energy criterion in 5 different configurations of the molecules adsorbed on the nanotube. Our computer simulations have found that the preferential adsorption site of the molecule on the nanotube surface is the parallel configuration for BT and DBT, and at one nanotube end for the T fragment, with all cases having physical interactions. The polarity exhibits an increase which favors the possible dispersion, provided the electrons are polarized. The nanostructure functionalization increases the chemical reactivity which in turn enhances interactions between the molecule and the nanotube. The BNNT-dibenzothiophene work function reduction as compared with the pristine case yields the improvement of the field emission properties.

Keywords: Boron Nitride nanotubes, Thiophene, Benzothiophene, Dibenzothiophene, Work function, DFT theory

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1 Introduction

The prediction of boron nitride nanotubes (BNNTs) published by Rubio et al. in 1994 [1] and the corresponding synthesis by Chopra et al. in 1995 [2] have motivated interest in these nanostructures. On the other hand the possible sample preparation with particular characteristics has been demonstrated: short length and open ends. These kinds of systems are suitable for biological applications [3] because they are soluble in water [4] and have prominent anticancer properties provided that they exhibit low toxicity [5,6]. Nanotube surface functionalization allows the fabrication of devices such as glucose biosensors [7] and visible light emitting diodes [8]. Taking into account the above mentioned facts it is required to continue exploring the nanotube surface and ends (because of dangling bonds) in the context of covalent or non-covalent functionalization with different functional groups or molecules to tailor electronic properties. Theoretical reports [9-14] have shown variations in the electronic and magnetic properties of both nanotubes and nanosheets made up of BN when these structures interact with organic molecules or functional groups. On the other hand note that aromatic molecules such as thiophene (T; C_4H_4S), benzothiophene (BT; C_8H_6S) and dibenzothiophene (DBT; $C_{12}H_8S$), which belong to the heterocyclic molecules, are present in petroleum production [15,16]. These molecules are highly reactive since the sulfur and adjacent carbons 1 and 2 (Fig. 1) exhibit delocalized electrons. Because of these it is possible to change the nanotube electronic properties in order to search for technological applications. In this work we analyze the surface and end functionalization effects on the structural (bond length and nanotube diameter) and electronic (polarity, chemical potential and work function which are important parameters for the device design) properties of single wall boron nitride

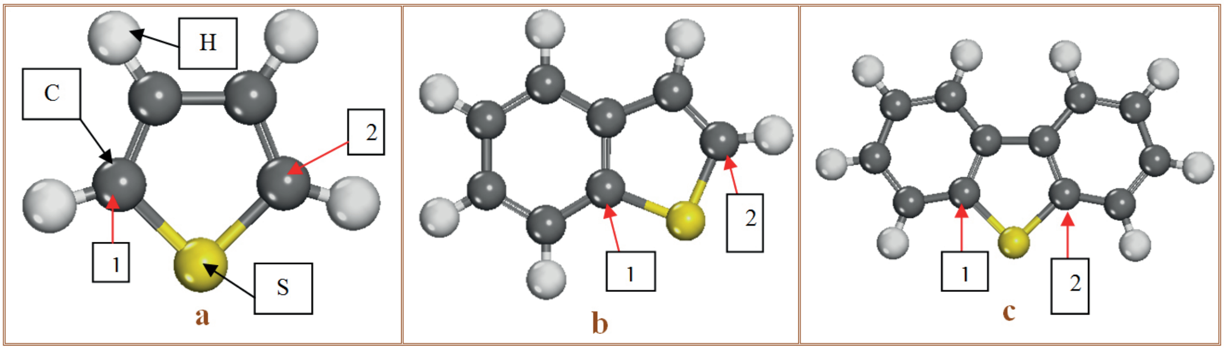


Figure 1: We display the structures of the heterocyclic molecules in **a**) thiophene, in **b**) benzothiophene and in **c**) dibenzothiophene. 1 and 2 are for adjacent carbons.

nanotubes of chirality (5,5). The functionalization of BNNTs is carried out with molecules that modify electronic properties and improve applications as reported in the literature [17-19]. The choice of (5,5) chirality is because this structure exhibits a strain energy of 0.123 eV/atom which is a low energy as compared with other chiralities. This energy value indicates that the nanostructure may easily phase transform from 2D to 1D [20].

Table 1: HOMO—LUMO gap Vs. Functionals for BNNT.

Functional	**HOMO-LUMO Gap** (eV)
[a]PW91	4.72
[a,b]BP	4.73
[c]PBE	4.70
[b,d]BLYP	4.72
[e]BOP	4.75
[a,b,f]VWN-BP	4.73
[g]RPBE	4.74
[h]HCTH	4.78

[a] J. P. Perdew, Y. Wang, Phys. Rev. B 45, 13244 (1992)
[a,b] A. D. Becke, J. Chem. Phys. 88, 2547 (1988)
[c] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)
[b,d] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 37, 786 (1988)
[e] T. Tsuneda, T. Suzumura, K. Hirao, J. Chem. Phys. 110, 10664 (1999)
[a,b,f] S. J. L. Vosko, Wilk, M. Nusair, Can. J. Phys. 58, 1200 (1980)
[g] B. Hammer, L. B. Hansen, J. K. Norskov, Phys. Rev. B 59, 7413 (1999)
[h] Reference 21.

2 Simulation Models and Methods

First principles total energy calculations are performed to investigate the interactions of (5,5) BNNTs with thiophenes. Studies take into account the Hamprecht-Cohen-Tozer-Handy (HCTH) [21] functional within the generalized gradient approximation and the all-electron DNP base function which includes double polarization (this uses the *p* orbital of the hydrogen and *d* orbital of B, N, C and S) [22] as implemented in the DMol^3 quantum chemistry code [23]. The HCTH functional has been used because this yields good results when compared with experimental data, Table 1. To determine the interaction distance between the thiophenes and the nanotube (Fig. 1) we have explored 5 different geometrical configurations: in the *first* the thiophene fragment is directed towards the nitrogen atom, in the *second* the fragment is oriented towards the boron atom, the *third* configuration is obtained when the thiophene is placed perpendicularly to the central hexagon of the nanotube surface, in the *fourth* the thiophene is placed parallel to the central hexagon of the nanotube surface and in the *fifth* the fragment is oriented perpendicularly to one of the nanotube ends. Charge neutrality and multiplicity 1 have been considered for the aromatic molecules, the BNNT and the BNNT-thiophenes systems. We study the properties of the (5,5) chirality nanotube of length 1.32 nm and diameter of 0.76 nm with hydrogenated open ends. The NT contains a total of 120 atoms (50 N, 50 B and 20 H). The interacting molecules are: thiophene (T; C_4H_4S), benzothiophene (BT; C_8H_6S) and dibenzothiophene (DBT; $C_{12}H_8S$).

The energy gap is determined as the difference between the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) orbital energies. The molecule energy adsorption on the BN nanotubes is defined as: Ead = E[(BNNT + X) – E(BNNT) – E(X); X = T, BT and DBT]. To measure the chemical reactivity we determine the chemical potential as the arithmetic average (HOMO+LUMO)/2 provided that in the free electron gas this is equal to the Fermi level and it is considered as the center of the energy gap [24]. The work function is defined as the minimum energy required to remove an electron from a solid to a point immediately outside the solid surface or the energy needed to move an electron from the Fermi energy level into vacuum. This work function is

Table 2: The table shows the total energy (a.u,) Vs. configurations for BNNT—thiophenes systems.

Configuration	BNNT-thiophene	BNNT-Benzothiophene	BNNT-Dibenzothiophene
1	-4549.0916081	-4702.7368768	-4856.3891490
2	-4549.0905577	-4702.7349402	-4856.3881220
3	-4549.0906004	-4702.7361193	-4856.3900556
4	-4549.0937785	-4702.7484659	-4856.3943013
5	-4549.0995075	-4702.7447881	-4856.3902014

determined as the energy difference between the vacuum level (LUMO orbital) and the Fermi level (chemical potential). The molecular electrostatics potential surfaces (MEPs) are calculated as described in the literature [25]. These surfaces are usually associated with the lone pairs of the more electronegative atoms.

An orbital cut off distance of 0.37 nm is used for T, BT and DBT and 0.34 nm for BNNT-X; X = T, BT and DBT on the base function with a tolerance of 2.0×10^{-5} Ha for the total energy convergence. The structural stability was obtained by applying the non-complex vibration frequency [26].

3 Results and Discussion

The open ends of BN nanotubes saturated with hydrogen atoms are systems suitable for molecular simulations which have attracted the attention of the scientific community as was shown by Hao et al. [27] in 2006. In the work the authors investigated magnetic and electronic properties. In our studies we shall explore nanotubes in the armchair configuration, that is, structures with (5,5) chirality having both ends saturated with hydrogen atoms and interacting with the following molecules: thiophene (T; C_4H_4S), benzothiophene (BT; C_8H_6S) and dibenzothiophene (DBT; $C_{12}H_8S$). The main purpose of this work is to investigate the structural and electronic properties of the nanotube systems, to determine changes in the electronic properties and search for applications. The convenience of studying these systems has been discussed in a recent report [28] where it is indicated that the energy gap of the nanotubes with Hamada indices (n,n) are the most stable. In addition it is possible to synthesize tubular structures open ends [1]. Moreover BNNTs of short length are suitable for functionalization with polymers and consequently they may be applied in biomedicine and in the formation of composites with high mechanical resistance [3,4].

3.1. Structural properties

The geometric optimization (Table 2) is done using the criteria established previously. Results indicate that the atomic structure of the interaction between the BNNT and the T fragment is *configuration 5* in the most stable state, that is, the geometry where the interaction is at one nanotube end with a separation distance of 4.07 and 3.92 Å (Fig. 2a). The nanotube retains the B-N 1.45 Å bond length of the pristine BNNT structure. One effect of the interaction is the contraction on the order of 0.01 nm in the nanotube diameter; meanwhile the T geometrical parameters before and after the interactions exhibit no changes, Table 3a. The interaction of the BNNT surface with the BT fragment yields a geometry (configuration 4) parallel to that of the minimum energy. The separation distance is 3.74 Å (this distance is the separation between the BNNT boron atom and the carbon atom 1, Fig. 2b). Similarly the B-N separation distance is 1.45 Å, however the BT structural parameters remain unchanged (Table 3a). Finally the interactions between the BNNT and DBT display the same geometry as that of the ground state (configuration 4) with a separation distance of 3.85 Å (this distance is between DBT S atom and the BNNT surface N atom, Fig. 2c). The DBT structural parameters are unchanged in the presence of interactions. Similar structural parameters are found in the interactions between DBT and carbon nanotubes (CNTs) with an interaction distance of 3.525 Å for the (7,7) armchair model and of 3.485 Å for the (10,5) chiral nanotube [29] structure.

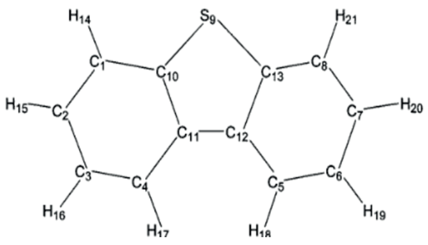
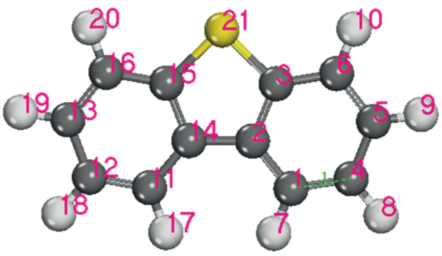
3.2 Electronic properties

The interaction energy of the BNNTs with T, BT or DBT is weak which yields physisorptions (Table 4). A similar phenomenon is observed in the dibenzothiophene adsorption on armchair (7,7) carbon nanotubes [30]. As indicated by the adsorption energy the interactions are weak (non-covalent interaction); on the other hand, the molecular electrostatic potentials (MEPs) (Fig. 3b and 3d) indicate the possible electronic charge distribution between the nanotube and the molecule. It is found that there is a surface charge transfer in BNNT-BT and BNNT-DBT. Meanwhile in the BNNT-T system the charge transference takes place between the thiophene H atoms and the saturating H atoms at the nanotubes ends. This is in agreement with the dipole moment vector direction (Fig. 4). However in literature reports on MEPs of the CNT-DBT system, no charge transference is found [30]. It is important to remark that the charge of the MEPs is mostly localized at the nitrogen atoms, which resemble the pristine BNNT. On the other hand, the systems studied systems – thiophenes (Fig. 5), BNNT-T (Fig. 6a), BNNT-BT (Fig. 6b), BNNT-DBT (Fig. 6c) and pristine BNNT (Fig. 7) – exhibit a semiconductor behavior with energy gap values (HOMO-LUMO energy difference) of 4.56 (T), 3.74 (BT), 3.39 (DBT), 4.55 (BNNT-T), 3.72 (BNNT-BT), 3.42 (BNNT-DBT) and 4.78 (BNNT) eV (Table 4). It is apparent that the system with DBT exhibits a gap reduction. In contrast the polarity is slightly increased form 0 D for the pristine BNNT, with a covalent behavior, to a polarity of 0.17 for BNNT-T, 0.66 for BNNT-BT and 0.69 D for BNNT-DBT. The

Table 3a: We report the optimum geometrical parameters for the thiophenes.

Bond length (Å)	Thiophene	Benzothiophene
C-H	1.087	1.09
C-C	1.42	1.40
C C	1.37	1.42
C-S	1.71	1.73

Table 3b: We report the optimum geometrical parameters for the dibenzothiophene.

				
	Ground state*	Exp**		Ground state
R(C1-C10)	1.397	1.386	R(C_{16}-C_{15})	1.396
R(C1-C2)	1.392	1.384	R (C_{13}-C_{16})	1.39
R(C2-C3)	1.404	1.385	R (C_{13}-C_{12})	1.401
R(C3-C4)	1.390	1.370	R (C_{11}-C_{12})	1.387
R(C4-C11)	1.403	1.392	R (C_{11}-C_{14})	1.401
R(S9-C10)	1.768	1.74	R (S_{21}-C_{15})	1.746
R(C10-C11)	1.413	1.409	R(C_{15}-C_{14})	1.412
R(C11-C12)	1.455	1.441	R (C_{14}-C_{2})	1.446
R(C1-H14)	1.086		R (C_{16}-H_{20})	1.089
R(C2-H15)	1.087		R (C_{13}-H_{19})	1.090
R(C3-H16)	1.086		R (C_{12}-H_{8})	1.090
R(C4-H17)	1.087		R(C_{11}-H_{17})	1.089

* Reference [32]; ** Reference [33].

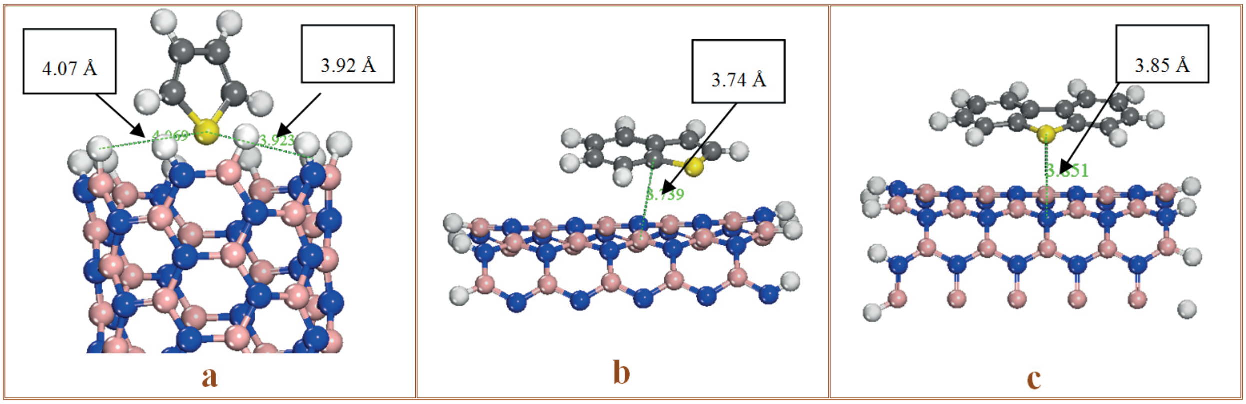


Figure 2: We show the optimized distances in the BNNT and **a**) thiophene, **b**) benzothiophene, **c**) dibenzothiophene structures.

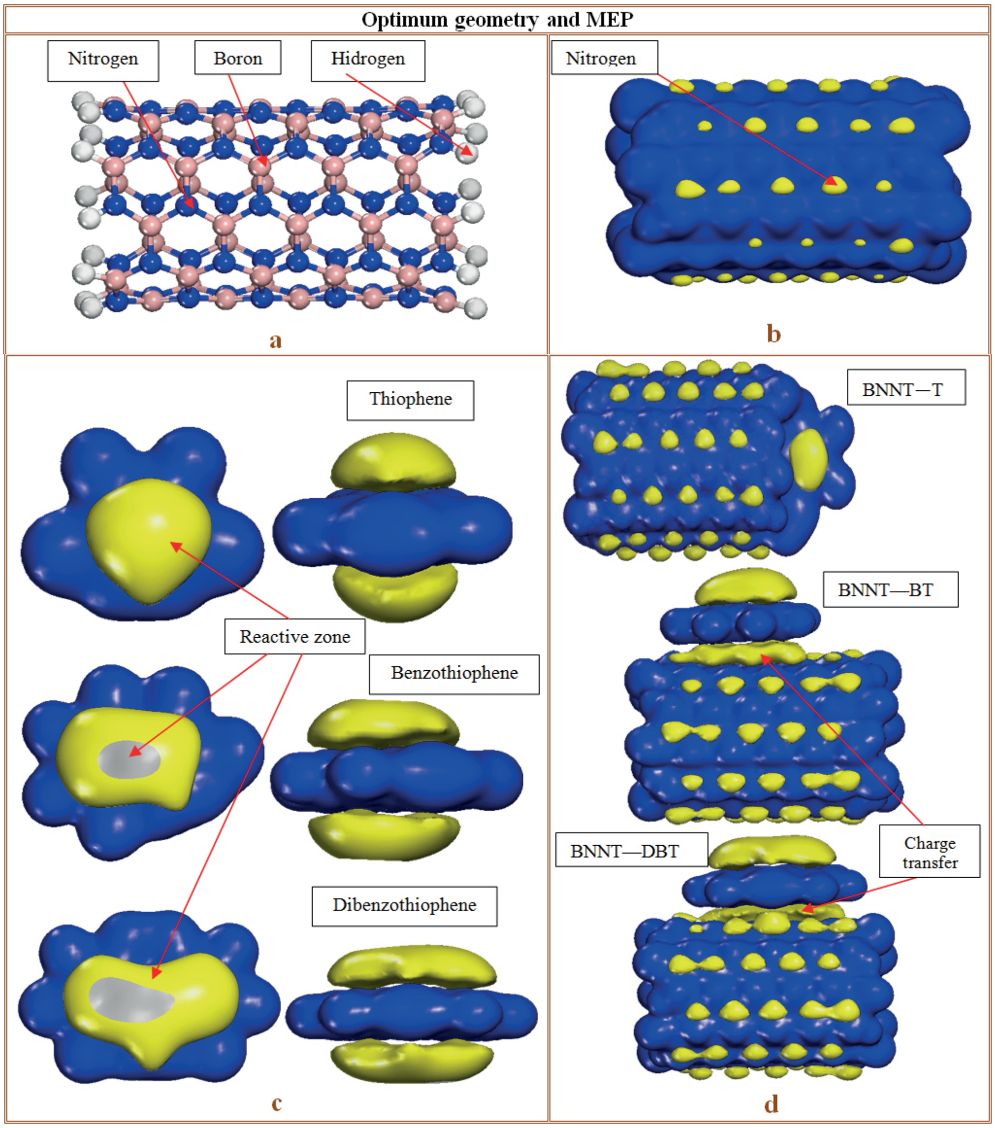


Figure 3: The figure displays in **a**) the optimized geometries for BNNT, **b**) the MEP for BNNT, **c**) the MEP for thiophenes, **d**) BNNT—thiophenes system in the most stable configuration. The blue color stands for the positive charge zone and the yellow color for the negative charge zone.

Table 4: The table reports the bond length (Å), HOMO—LUMO gap (eV), Fermi Energy Level (eV), Dipolar moment (eV), Work function (eV), and energy adsorption (eV) for BNNT—thiophenes.

Nanotubes	**Bond length (Å)** B—N	**HOMO—LUMO gap**	**Energy Fermi level**	**Dipolar Moment**	**Work Function**	**Energy adsorption**
BNNT experimental		4-5 [1,35-38]				
(5,5) BNNT	1.45	4.78	-3.65	0.017	2.3	
Thiophene		4.56	-3.53	0.21	3.43	
Benzothiophene		3.74 3.32 [29]	-3.56	0.38	1.87	
Dibenzothiophene		3.39	-3.69	0.43	1.69	
(5,5) BNNT—T	1.45	4.55	-3.33	0.17	2.27	-0.49
(5,5) BNNT—BT	1.45	3.72	-3.14	0.66	1.85	-0.53
(5,5) BNNT—DBT	1.45	3.42	-3.30	0.69	1.71	-0.46

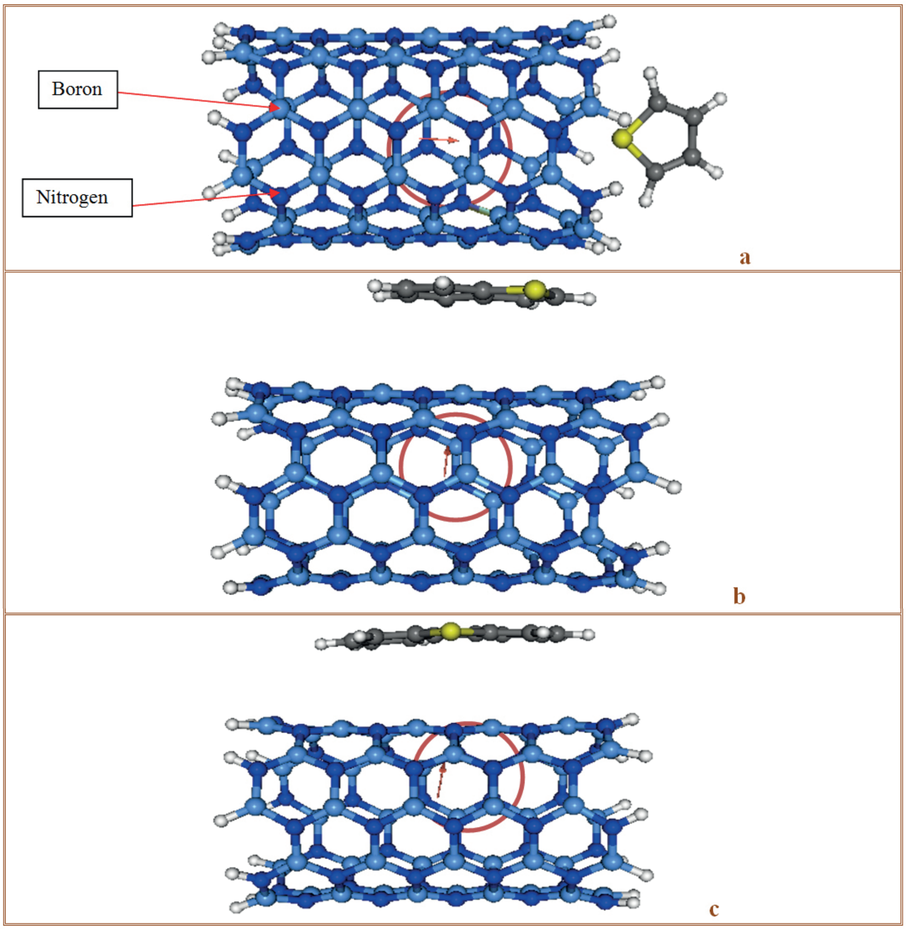


Figure 4: The figure displays the dipolar moment indicating the direction of the charge distribution **a**) for the BNNT—thiophene, **b**) for the BNNT—benzothiophene, **c**) for the BNNT—dibenzothiophene at the level HCTH/6-31g(d) [21,38] and plotted by GaussSum [39].

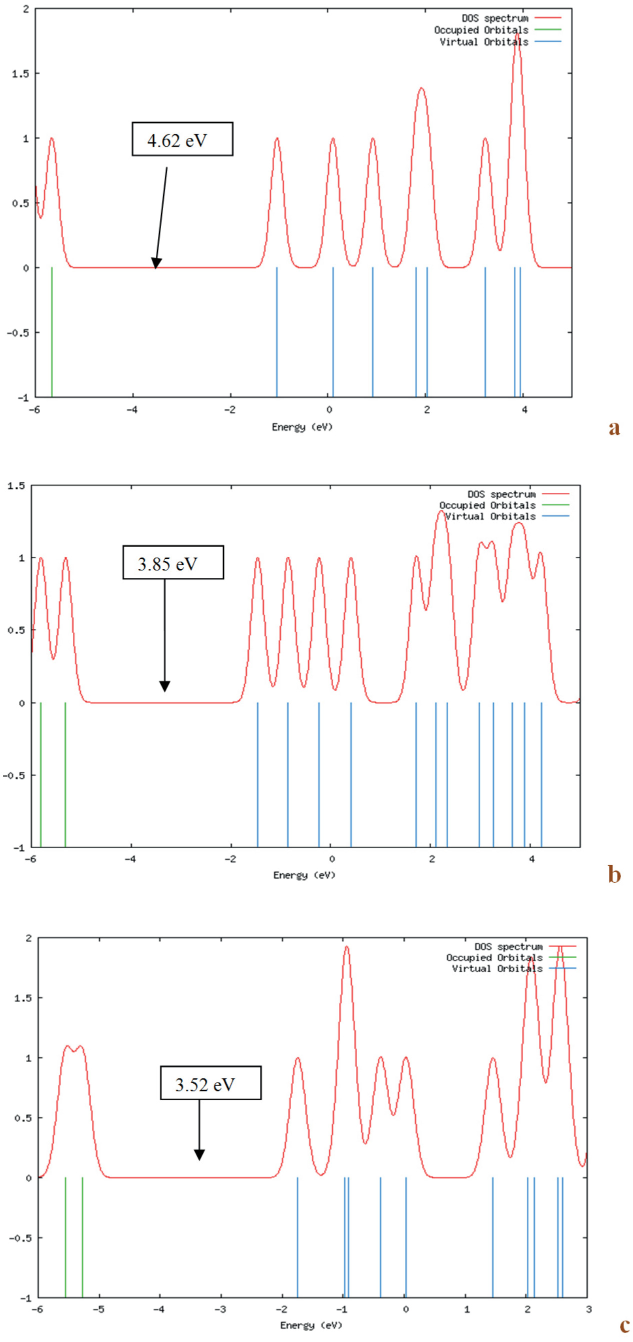


Figure 5: We plot the total DOS (Energy eV Vs States/eV) for thiophene **a**), benzothiophene **b**), dibenzothiophene **c**) at the level HCTH/6-31g(d) [21,38] and plotted by GaussSum [39].

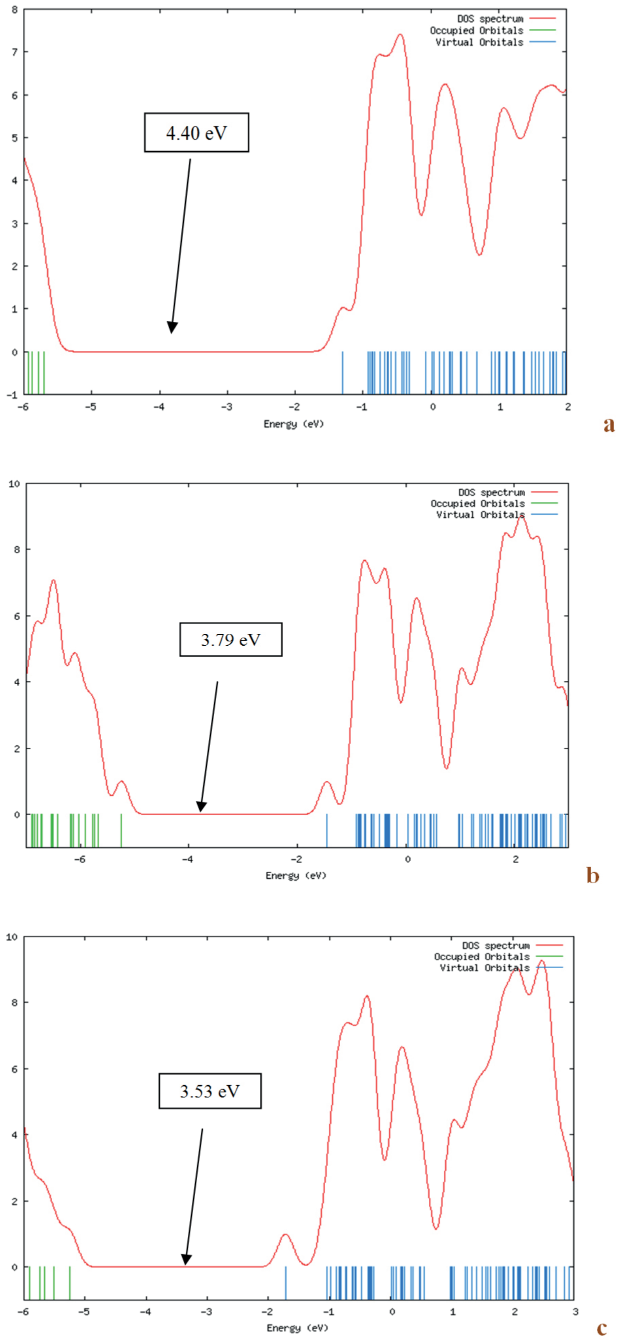


Figure 6: We show the total DOS (Energy eV Vs States/eV) for BNNT—thiophene **a**), BNNT—benzothiophene **b**), BNNT—dibenzothiophene **c**) at the level HCTH/6-31g(d) [21,38] and plotted by GaussSum [39].

charge distribution is localized near the interaction zone between the nanotube and the thiophenes as indicated by the surface of the MEPs (Fig. 1d). The polarity increase is also obtained when the BNNTs interact with other molecules [11,17-19]. The nanotubes functionalized with BT and DBT exhibit a reduced work function from 0.45 and 0.59 eV to 1.85 and 1.71 eV, respectively, as indicated in Table 4. Therefore the presence of adsorbates on the surface of the functionalized nanotubes offers good conditions to improve field emission properties (FEPs). Another argument for the possibility of improving the FEPs is based on the chemical potential value (Table 4), which exhibits a small increase (-3.33 eV for the BNNT-T; -3.14 eV for the BNNT-BT and -3.30 eV for the BNNT-DBT

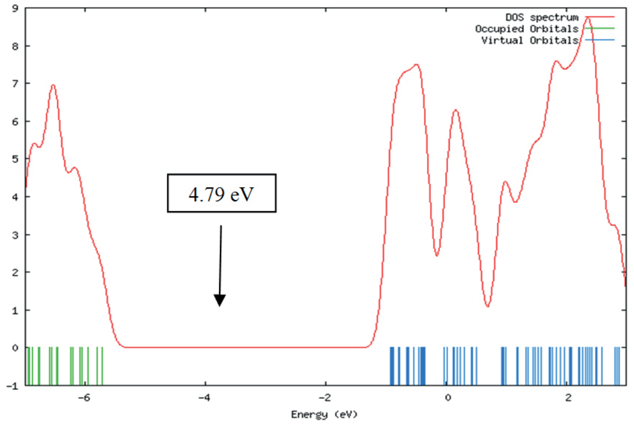


Figure 7: We display the DOS (States/eV Vs Energy eV) for pristine BNNT at the level HCTH/6-31g(d) [21,38] and plotted by GaussSum [39].

systems) inducing a more favorable interaction in these systems. Finally the electrical conductivity changes are calculated with the formula $\sigma \alpha \exp(-E_g k^{-1} T^{-1})$, where E_g is the energy gap of the HOMO-LUMO difference, k the Boltzmann constant and T (K) the temperature [31]. For a given temperature the BNNT-BT and BNNT-DBT structures display high conductivity provided that the energy gaps are 3.72 and 3.42 eV, while the BNNT and BNNT-T systems with large energy gap exhibit kinetic stability with low electrical conductivity.

4 Conclusions

We have presented ab-initio studies of the interactions of TF, BT and DBTF with armchair boron nitride nanotubes (BNNTs). The associated systems display physical interactions and the functionalization occurs at different NT sites: in the BNNT-TF system this takes place at the NT ends, while in the BNNT-BTF and BNNT-DBTF structures it occurs on the surfaces. The interactions induce possible charge transference as indicated by the MEP surface. The decrease of the chemical potential indicates that the interactions are favored in every case. The work function decrease of the BNNT-BTF (1.72 eV) and BNNT-DBTF (1.42 eV) as compared with the pristine BNNT indicates that the systems we have investigated are suitable for applications in the fabrication of displays, which may be studied according to molecular conduction [32] and by FEPs modification.

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References

[1] Rubio A., Corkill J. L., Cohen M., Theory of graphitic boron nitride nanotubes, Phys. Rev. B, 1994, 49, 5081-5084

[2] Chopra N. G., Luyken R. J., Cherrey K, Crespi V. H., Cohen M. L., Louie S. G., Zetl A., Boron Nitride Nanotubes, Science 1995, 269, 966-967

[3] Golberg D., Bando Y., Unique morphologies of boron nitride nanotubes, Appl. Phys. Lett. 2001, 79, 415-417

[4] Huei Lee C., Zhang D., Khin Yap Y., Functionalization, Dispersion, and Cutting of Boron Nitride Nanotubes in Water, J. Phys. Chem. C 2012, 116, 1798- 1804

[5] Raffa V., Riggio C., Smith M. W., Jordan K. C., Cao W., Cuschieri A., BNNT-mediated irreversible electroporation: its potential on cancer cells, Technol. Cancer Res. Treat. 2012, 11, 459-465

[6] Ciofani G., Raffa V., Menciassi A., Cuschieri A., Boron nitride nanotubes: an innovative tool for nanomedicine, Nano Today 2009, 4, 8-10

[7] Wu J., Yin L., Platinum Nanoparticle Modified Polyaniline-Functionalized Boron Nitride Nanotubes for Amperometric Glucose Enzyme Biosensor, ACS Appl. Mater. Interfaces 2011, 3, 4354-4362

[8] Gao Zh., Zhi Ch., Bando Y., Golberg D., Serizawa T., Noncovalent Functionalization of Disentangled Boron Nitride Nanotubes with Flavin Mononucleotides for Strong and Stable Visible-Light Emission in Aqueous Solution, ACS Appl. Mater. Interfaces 2011, 3, 627-632

[9] Zhi C. Y., Bando Y., Tang C., Honda S., Sato K., Kuwahara H., Golberg D., Characteristics of Boron Nitride Nanotube–Polyaniline Composites, Angew. Chem. Int. Ed. 2005, 44, 7929-7932

[10] Xie S. Y., Wang W., Fernando K. A. S., Wang X., Lin Y., Sun Y. P., Solubilization of boron nitride nanotubes, Chem. Commun. 2005, 29, 3670-3672

[11] Rodríguez Juárez A., Chigo Anota E., Hernández Cocoletzi H., Flores Riveros A., Adsorption of chitosan on BN nanotubes: A DFT investigation Appl. Surf. Sci. 2013, 268, 259-264

[12] Saikia N., Pati S. K., Deka R. C., First principles calculation on the structure and electronic properties of BNNTs functionalized with isoniazid drug molecule, Appl. Nanosci. 2012, 2, 389-400

[13] Chigo Anota E., Hernández Rodríguez L. D., Hernández Cocoletzi G., Influence of point defects on the adsorption of chitosan on Graphene-like BN nanosheets, Graphene 2013, 1 (2), 124-130

[14] Chigo Anota E., Rodríguez Juárez A., Castro M., Hernández Cocoletzi H., A density functional theory analysis for the adsorption of the amine group on Graphene and Boron Nitride Nanosheets,J. Mol. Model. 2013, 19 (1), 321-328

[15] McKee H. C., Herndon L. K., Withrow J. R., Estimation of Thiophene in Gasoline, Anal. Chem. 1948, 20 (4), 301-303

[16] Moore R. J., Greensfelder B. S., The Catalytic Synthesis of Benzothiophene, J. Am. Chem. Soc. 1947, 69 (8), 2008-2009

[17] Chigo Anota E., Hernández Cocoletzi G., GGA-based analysis of the metformin adsorption on BN Nanotubes, Physica E 2014, 56, 134-140

[18] Chigo Anota E., Hernández Cocoletzi H., Salazar Villanueva M., García Toral D., First-principles investigation of the interaction between BN, SiC and ZnO Nanotubes —BaTiO3, Superlatt. Microstruct. 2013, 63, 298-305

[19] Chigo Anota E., Hernández Cocoletzi G., Sánchez Ramírez J. F., Armchair BN Nanotubes — Levothyroxine interactions: A Molecular Study, J. Mol. Model. 2013, 19, 4991-4996

[20] Baumeier B., Krüger P., Pollmann J., Structural, elastic, and electronic properties of SiC, BN, and BeO nanotubes, Phys. Rev. B 2007, 76, 085407(1)-(10)

[21] Boese A. D., Handy N. C., A new parametrization of exchange–correlation generalized gradient approximation functionals, J. Chem. Phys. 2001, 114, 5497-5503

[22] Delley B., An All-Electron Numerical Method for Solving the Local Density Functional for Polyatomic Molecules, J. Chem. Phys. 1990, 92, 508-517

[23] Delley B., From molecules to solids with the DMol3 approach, J. Chem. Phys. 2000, 113, 7756-7764

[24] Geerlings P., De Proft F., Langenaeker W., Conceptual Density Functional Theory, Chem. Rev. 2003, 103, 1793-1874

[25] Chigo Anota E., Ramírez Gutiérrez R. E., Pérez Sanchéz F. L., Sanchéz Ramírez J. F., Structural Characteristics and Chemical Reactivity of Doped Graphene Nanosheets, Graphene 2013, 1 (1), 31-36

[26] Foresman JB, Frisch Æ. Exploring Chemistry with Electronic Structure Methods, 2nd ed., Gaussian Inc., USA, 1996

[27] Hao S., Zhou G., Duan W., Wu J., Gu B. L., Tremendous spin-splitting effects in open boron nitride nanotubes: application to nanoscale spintronic devices, J. Am. Chem. Soc. 2006, 128, 8453(1)-(8)

[28] Xiang H. J., Yang J., Hou J. G., Zhu Q., First-principles study of small-radius single-walled BN nanotubes, Phys. Rev. B 2003, 68, 035427(1)-(5)

[29] Gómez B., Martínez Magadán J. M., A theoretical study of dibenzothiophene absorbed on open-ended carbon nanotubes, J. Phys. Chem. B 2005, 109, 14868-14875

[30] Li S. Semiconductor Physical Electronics, 2nd ed., Springer, USA, 2006

[31] Matsunaga N., Molecular Conduction Characteristics from the Intrinsic Molecular Properties, J. Comp. Theor. Nanosci. 2006, 3, 1-7

[32] Yeon Lee S., Density Functional Theory Calculation of Molecular Structure and Vibrational Spectra of Dibenzothiophene in the Ground and the Lowest Triplet State, J. Phys. Chem A 2001, 105, 8093-8097

[33] Schaffrin R., Trotter J., Structure of dibenzothiophene, J. Chem. Soc. A 1970, 1561-1565

[34] Radosavljevi M., Appenzeller J., Derycke V., Martel R., Avouris Ph., Loiseau A., Cochon J. L., Pigache D., Electrical properties and transport in boron nitride nanotubes, Appl. Phys. Lett. 2003, 82, 4131-4133

[35] Lauret J. S., Arenal R., Ducastelle F., Loiseau A., Cau M., Attal-Tretout B., Rosencher E., Goux-Capes L., Optical transitions in single-wall boron nitride nanotubes, Phys. Rev. Lett. 2005, 94, 37405(1)-(4)

[36] Cumings J., Zettl A., Field emission and current-voltage properties of boron nitride nanotubes, Solid State Commun. 2004, 129, 661-664

[37] Ishigami M., Sau J. D., Aloni S., Cohen M. L, Zettl A., Observation of the Giant Stark Effect in Boron-Nitride Nanotubes, Phys. Rev. Lett. 2005, 94, 56804(1)-(4)

[38] Gaussian 09, Revision C.01, Frisch M. J., Trucks G. W, Schlegel H. B., Scuseria G. E., Robb M. A, Cheeseman J. R., Scalmani G., Barone V., Mennucci B., Petersson G. A., Nakatsuji H., Caricato M., Li X., Hratchian H. P., Izmaylov A. F., Bloino J., Zheng G., Sonnenberg J. L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery, Jr. J. A., Peralta J. E., Ogliaro F., Bearpark M., Heyd J. J., Brothers E., Kudin K. N., Staroverov V. N., Keith T., Kobayashi R., Normand J., Raghavachari K.,. Rendell A, Burant J. C., Iyengar S. S., Tomasi J., Cossi M., Rega N., Millam J. M., Klene M., Knox J. E., Cross J. B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R. E., Yazyev O., Austin A. J., Cammi R., Pomelli C., Ochterski J. W., Martin R. L., Morokuma K., Zakrzewski V. G., Voth G. A., Salvador P., Dannenberg J. J., Dapprich S., Daniels A. D., Farkas O., Foresman J. B., Ortiz J. V, Cioslowski J., Fox D. J., Gaussian, Inc., Wallingford CT, 2010

[39] O'Boyle N. M., Tenderholt A. L., Langner K. M., cclib: A library for package-independent computational chemistry algorithms, J. Comp. Chem. 2008, 29, 839-845