RESULTS AND DISCUSSION

Chapter I. Theoretical study on structural and electronic properties of the BN-doped Carbon Nanotubes grafted with N-nucleophiles

1. Structural geometry

The charge distribution and distances of B-C, N-C, C-C bonds of BN-doped SWCNT are shown in Fig. 9. The charge ranges between -0.586***e*** and +0.832***e*.** The nitrogen atom has the highest negative charge while the boron atom has the highest positive charge. Table 2 shows the optimized structural parameters for BN-doped SWCNT and the corresponding adsorption systems (Fig. 10).

1.1 Local structure of BN-doped SWNT

The optimized B-N, B-C1 and B-C2 distances of the BN-doped SWNCT are 1.46, 1.53, and 1.51 Å, respectively, showing the elongation of bond distances compared to the C-C bond (1.43 Å) in the undoped SWCNT. Moreover, the ∠N-B-C1, ∠N-B-C2 and ∠C1-B-C2 angles are 118.0, 118.6 and 114.7°, respectively, which are relatively smaller than those ∠C-C-C angles in the undoped SWCNT (~120°). The changes of the structure at the BN-doped position compared to the undoped SWCNT induce the less stabilization of sp^2 hybridization even though it is still preserved at this state. However, sp^2 hybridization could be changed to sp^3 hybridization when the adsorption processes of probed molecules take place.

1.2 Nitrogen nucleophiles attached on BN-doped SWCNT

In the *R-group*/BN-doped SWCNT systems, when the reaction takes place, the bond distances of the *R-group* and B (R-B) are in the range of 1.60-1.79 Å, depending upon the interaction strength, which, in most cases, is indicated by the stronger interaction, that results from the shorter bond distances. Furthermore, the

B-N, B-C1 and B-C2 bond distances are lengthened and lie in the rage of 1.52-1.57, 1.59-1.61 and 1.57-1.59 Å, respectively. It was found that these intra-atomic distances increase when the strong interaction of the R-group and BN-doped SWCNT formed. For example, guanidine shows the most strongest interaction to BN-doped SWCNT and gives the R-B, B-N, B-C1 and B-C2 of 1.61, 1.57, 1.61 and 1.59 Å, respectively, while m-nitroaniline (the less stable system) shows the corresponding distances of 1.79, 1.52, 159 and 1.57 Å, respectively. The other systems also show such behaviors depending on their binding energies.

To further explain in terms of hybridization, we consider the modification of angles around BN-doped region. In all cases, it is shown that the angle parameters of BN-doped SWCNT affected by the *R-group* are reduced and rather closed to the ideal tetrahedral geometry where each angle is 109.47°, indicating that such systems exhibit the sp^3 hybridization instead of the sp^2 hybridization.

2. Binding energy and pK_a

In this study, the chemical interactions of nitrogen nucleophiles (*R-group*) and BN-doped SWCNT are reported in terms of binding energy (E_b). Table 3 shows the corresponding binding energies for the systems that were studied. We found that the binding energies for all systems lie between -6.90 and -30.13 kcal/mol and are in the order of guanidine > arginine > ammonia > imidazole > chitosan > pyridine > m-nitroaniline. The adsorption of guanidine on BN-doped SWCNT is the most stable system with the corresponding binding energy of 30.13 kcal/mol while the adsorption of m-nitroaniline is the less stable system with the binding energy of only 6.90 kcal/mol. We found that the structures of adsorbed molecules as well as their intrinsic electronic properties play a vital role in the binding energy. We will discuss in more detail concerning the charge redistribution in electronic property section.

We also report the relationship of binding energy and pK_a of such complexes in Fig. 11. We found that the binding energy is directly proportional to the pK_a value, which indicates that the more basicity, the more binding energy.

Table 3 Interaction parameters between the BN-doped SWCNT and various N-nucleophiles

R-groups	pKa	Eb(kcal/mol)	E_g (eV)	ΔE_g (%)[a]
m-nitroaniline	2.47	-6.90	0.252	-41.7
pyridine	5.14	-16.32	0.347	-20.0
chitosan	6.50	-14.75	0.471	8.8
imidazole	6.95	-18.89	0.445	2.8
NH_3	9.30	-18.94	0.457	5.6
arginine	12.48	-28.57	0.459	6.1
guanidine	13.71	-30.13	0.445	6.5

[a] compared to the E_g value obtained from isolated BN-doped SWCNT of 0.43 eV

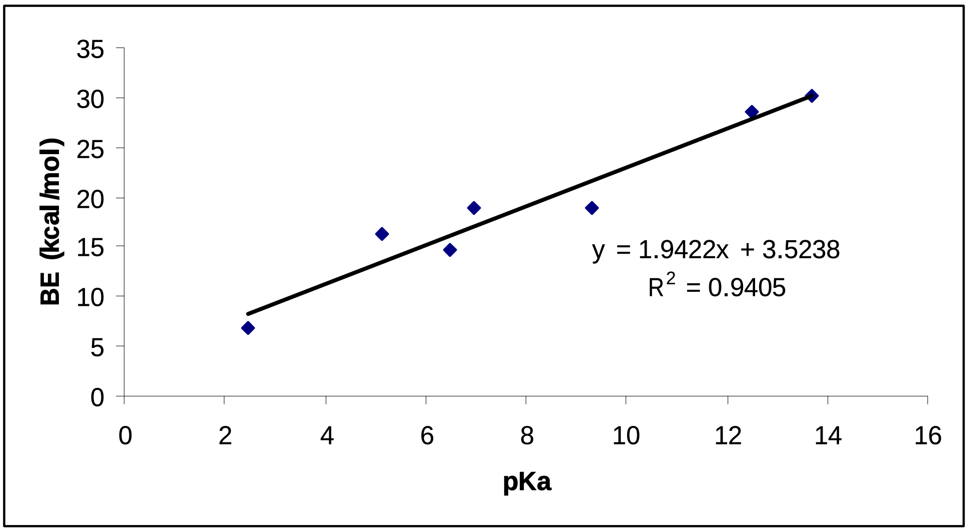


Figure 11 Correlation between binding energies and pK_a values of BN-doped SWCNT/N-nucleophiles complexes

3. Electronic properties

In order to evaluate the electronic properties of BN-doped SWCNT system as well as its interaction with the *R-groups*, we calculated the charge redistribution and their electronic density of states (DOSs).

3.1 Charge redistribution

Figs. 12-13 show the charge redistribution of some selected systems, including m-nitroaniline and pyridine complexes. The charge redistribution of all systems was derived from the Natural Population Analysis (NPA) procedure. The corresponding results were partitioned into the BN-doped SWCNT and N-nucleophile parts. The total charge of the BN-doped SWCNT part is negative (-0.28***e*** and -0.32***e*** for the m-nitroaniline and pyridine systems, respectively) while the total charge of the N-nucleophile part is positive (+0.28***e*** and +0.32***e*** for the m-nitroaniline and pyridine systems, respectively). Comparing with the isolated molecule, the total charge of aromatic ring in the complex systems is more positive, indicating that electrons of N-nucleophile ring were transferred to the BN-doped SWCNT. It can be expected that m-nitroaniline binds loosely to the BN-doped SWCNT because the NO_2 group withdraws electrons out of the aromatic ring and the NH_2 group, hence weakening the basicity of the N1 atom. The partitioning of charge distribution in the isolated m-nitroaniline molecule shows that the total charge distribution at the NO_2 group is negative (-0.24***e***) while it is positive and neutral at the aromatic ring (+0.24***e***) and the NH_2 group (0.00***e***), respectively. Instead, there is no electron withdrawing group attached to the pyridine ring, therefore, its N1 atom exhibits stronger base than that of m-nitroaniline.

In the cases of chitosan, imidazole and ammonia molecules, electrons are more localized at a specific region, giving rise to more electron donor ability to N1. For arginine and guanidine molecules, these molecules are quite similar due to their guanidinium group. Generally, guanidine prefers to behave in a resonance structure because of the conjugation between the double bond and the nitrogen lone pair electrons, thus, the positively charged guanidium ion structure is preferred and enhances the electron donor capability of N1.

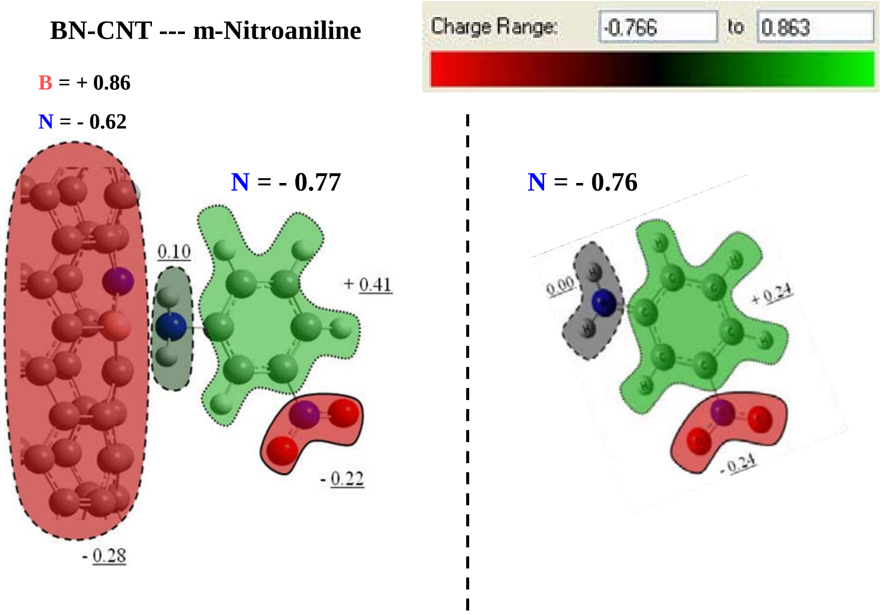


Figure 12 Charge distribution of isolated m-nitroaniline and m-nitroaniline complexed with BN-doped SWCNT

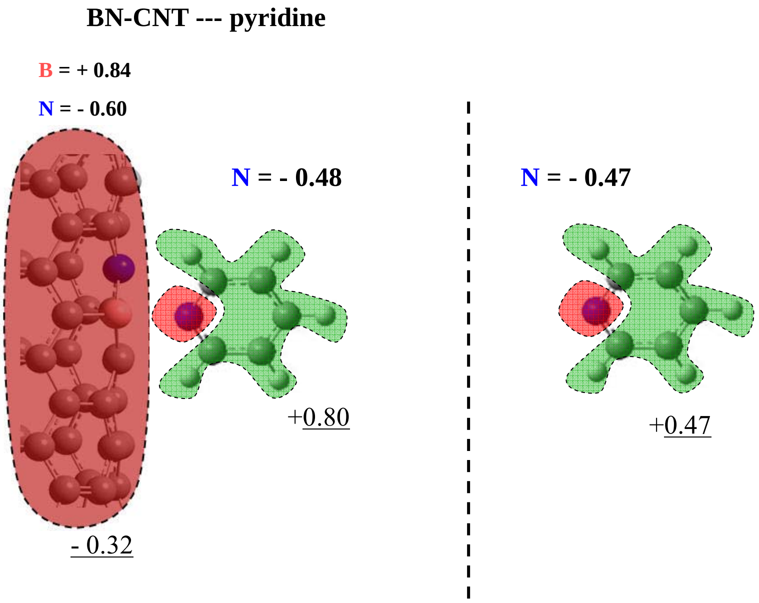


Figure 13 Charge distribution of isolated pyridine and pyridine complexed with BN-doped SWCNT

3.2 Energy gap and Densities of states

Table 3 shows the energy gap (E_g) of *R-group*/BN-doped SWCNT systems. The calculated E_g is correlated with the binding energy. The m-nitroaniline and pyridine perform well grafting molecules on BN-dope SWCNT. This is indicated by the smaller energy gaps of 0.25 and 0.35 eV, respectively, as compared to that of isolated BN-doped SWCNT of 0.43 eV. For the other cases, no significantly changes of the energy gaps can be observed. The charge redistribution can be found when the aromatic N-nucleophiles were attached to the BN-doped SWCNT. This, however, does not occur in non-aromatic N-nucleophiles and, therefore, there is no change in the energy gap. From these results, one can be expected that the pyridine derivatives may be useful for functionalization or modification of the BN-doped carbon-conducting materials for specific applications. This is due to their stability and conductivity of the complexes.

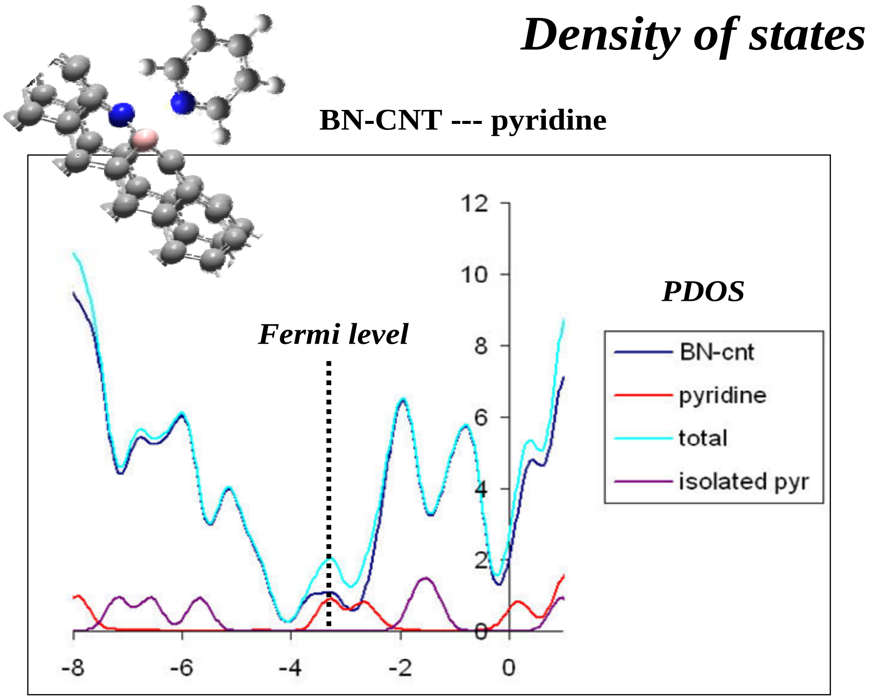


Figure 14 Partial density of states of pyridine complexed with BN-doped SWCNT

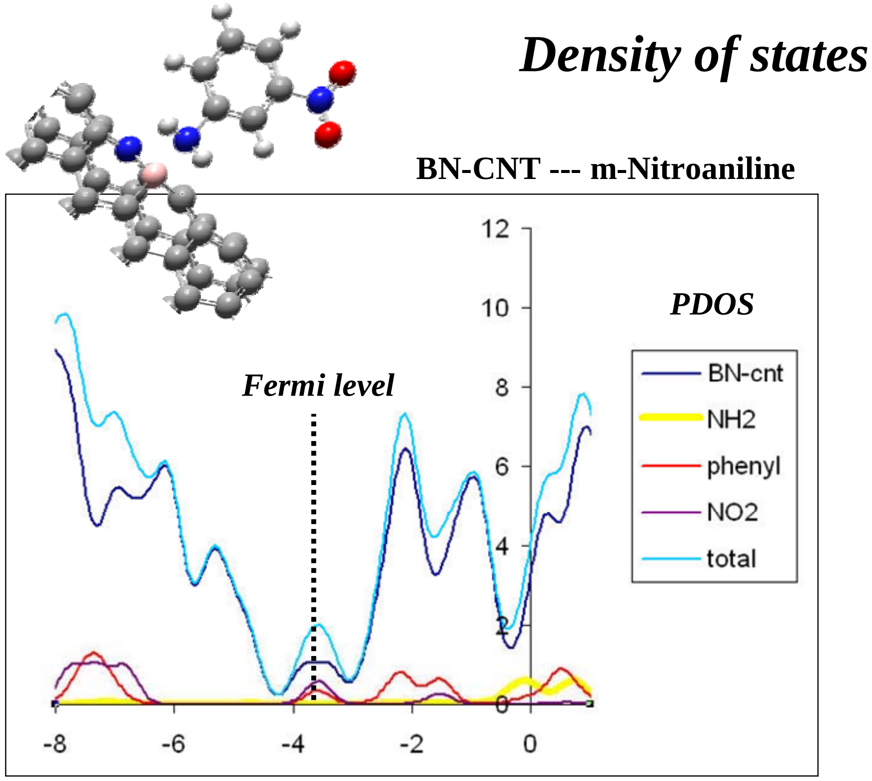


Figure 15 Partial density of states of m-nitroaniline complexed with BN-doped SWCNT

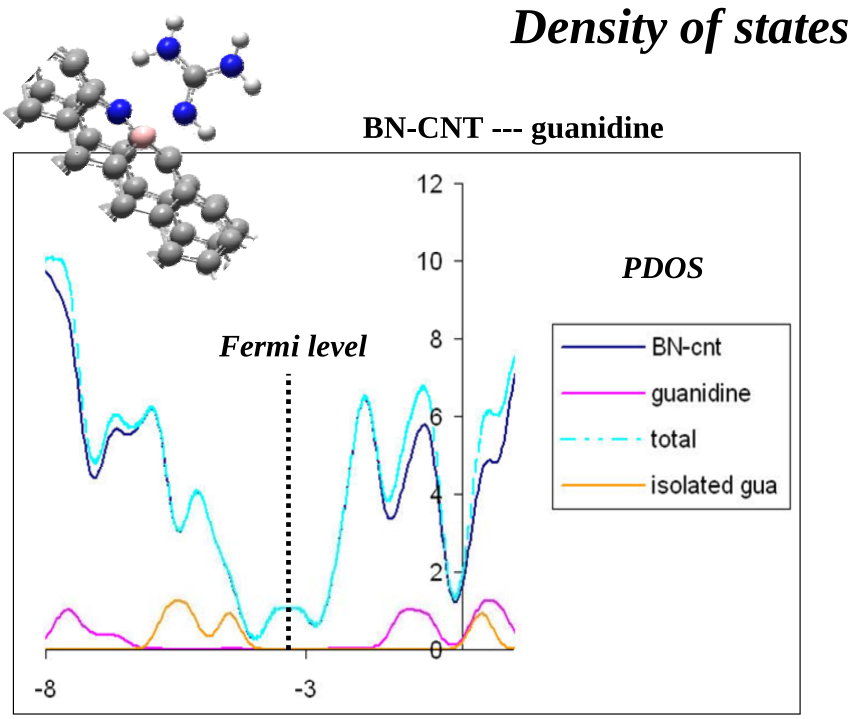


Figure 16 Partial density of states of guanidine complexed with BN-doped SWCNT

Figs. 14-16 show the plots of partial density of states of the BN-doped SWCNT grafted with pyridine, m-nitroaniline and guanidine and energy of states. The density of states in the Fermi level was shown in the vertically black dot line.

For the pyridine complex (Figure 14), the densities of states of the BN-doped SWCNT and pyridine were represented by blue and red lines, respectively. The total density of states, which is the summation of both the BN-doped SWCNT and pyridine, was shown in aqua line. At the Fermi level, it was found not only the density of state that belongs to the BN-doped SWCNT, but also the density of states contributed from pyridine. This is different to the isolated pyridine in which there is no state at the Fermi level for the reason that the gap between the HOMO and LUMO orbital energy is too large (3.99 eV). From this result, we might conclude that, when pyridine was attached with BN-doped SWCNT at a boron atom, it generates the states at the Fermi level of the complex, and thus increases the conductivity of the system.

The total density of states at the Fermi level increases by about 100% from that of isolated BN-doped SWCNT and the energy gap reduces by 20%.

For the m-nitroaniline complex (Figure 15), the densities of states of BN-doped SWCNT, NH_2, phenyl and NO_2 groups, were represented by blue, yellow, red and violet lines, respectively. Similar to pyridine complex, the total density of states increases when m-nitroaniline forms complex with the BN-doped SWCNT. The density of states at the Femi level was found in the complex of m-nitroaniline and the BN-doped SWCNT but not in the isolated molecules. It can be seen that all parts (NO_2, NH_2, and phenyl groups) of m-nitroaniline contribute to increase the total density of states at the Fermi level of the complex. This result might be one of the reasons to explain why the energy gap of m-nitroaniline decreases much more than that of pyridine (about 42%)

The guanidine is one of the non-aromatic N-nucleophiles that the energy gap is very slightly changed (increased less than 8% compared to that of isolated BN-doped SWCNT, 0.43 eV) after grafted to the BN-doped SWCNT. The density of states of the complex, BN-doped SWCNT and Guadinine were represented by aqua, blue, and pink lines respectively. The total density of states of the complex is solely contributed by the BN-doped SWCNT and still the same as in the isolated BN-doped SWCNT. Therefore, guanidine and other non-aromatic N-nucleophiles are not suitable for grafting with the BN-doped SWCNT for improving the conductivity of materials.

3.3 Energies and features of HOMO and LUMO orbitals of pyridine, m-nitroaniline, and their complex with BN-doped SWCNT

Figs. 17-18 show the energy levels and energy surfaces for HOMO and LUMO orbitals of pyridine, m-nitoaniline, and their complex with the BN-doped SWCNT . The diagrams show the reduction of an energy gap (E_g) when pyridine and m-nitroaniline form complexes with the BN-doped SWCNT. It can be seen that the HOMO orbitals of complexes are solely contributed by the BN-doped SWCNT while the LUMO orbitals are solely contributed by pyridine and m-nitroaniline. This suggests that there is no overlapping between π-orbitals of adsorbing molecules and the BN-doped SWCNT. The interaction between adsorbing molecules and the BN-doped SWCNT is just a weak σ-bond between lone pair electrons of the N atom and the empty p-orbital of the BN-doped SWCNT.

Chapter II. Theoretical study on structural and electronic properties of the BN-doped Fullerene grafted with heterocyclic N-nucleophiles.

1. Fullerene and BN-doped fullerene as reference systems

In the case of fullerene, we found that the average bond distances for hexagonal-hexagonal and hexagonal-pentagonal are 1.40 and 1.45 Å, respectively. The BN heteroatoms induce the local structural recreation around the BN substituted site, giving the BN, BC and NC distances of 1.44, 1.54 and 1.42 Å, respectively, resulting in a gradual upward shifted of the B atoms from the original C analogue.

The HOMO-LUMO energy gap obtained for fullerene was calculated to be 1.64 eV. The addition of BN heteroatoms into fullerene reduces the corresponding energy gap to 1.46 eV, which indicated an improvement for the electronic conductivity properties, albeit, a rather small alteration. The reduction of the energy gaps are in good agreement with literatures which indicated that the substitution of BN atoms to fullerene slightly reduces the energy gap ~0.2 eV.

Table 4 Relative energy gap reduction of systems compared to C_{60} (E_{gap} = 1.64 eV).

Systems	Relative energy gap reduction (eV)	Binding energies (kcal/mol)
C_{60}	-	-
$C_{58}BN$	0.18	-
$C_{58}BN$/**1**	1.03	-28.82
$C_{58}BN$/**2**	0.82	-29.95
$C_{58}BN$/**3**	1.23	-30.42
$C_{58}BN$/**1**/$C_{58}BN$	1.54	-52.32
$C_{58}BN$/**2**/$C_{58}BN$	1.41	-55.05
$C_{58}BN$/**3**/$C_{58}BN$	1.64	-56.69

Figs. 19-21 show the energy levels and gap energies of the HOMO & LUMO of complexed formation of $C_{58}BN$/**1**/$C_{58}BN$, $C_{58}BN$/**2**/$C_{58}BN$ and $C_{58}BN$/**3**/$C_{58}BN$ complexes including isolated fullerene, BN-doped fullerene ($C_{58}BN$), $C_{58}BN$/**1,** $C_{58}BN$/**2** and $C_{58}BN$/**3.** As for the isolated heterocyclic compounds, 2,6-diazanaphthalene, 3,8-diazaphenanthrene and 2,6-diazaanthracene interact with BN-doped fullerene on the boron atom as a positive charge into $C_{58}BN$/**1,** $C_{58}BN$/**2** and $C_{58}BN$/**3** respectively. The sequence of energy gaps (HOMO-LUMO) for 3,8-diazaphenanthrene, 2,6-diazanaphthalene and 2,6-diazaanthracene compounds (3.22, 2.97 and 2.30 eV, respectively) correspond with the sequence of energy gaps for $C_{58}BN$/**2,** $C_{58}BN$/**1** and $C_{58}BN$/**3** (0.82, 0.61 and 0.41 eV, respectively). This results show that the energy gap of heterocyclic compounds influences the energy gap of complexes occurring and that the nucleophile molecule donates electrons to a positive ion.

Furthermore, the corresponding calculated binding energies are -29.95, -28.82 and -30.42 kcal/mol, which are quite similar because the nucleophilities or basicities of each nucleophile is not significantly different. Not only that, the figures show the HOMO & LUMO level shifts all structures on the electron donation reaction of nucleophiles to a positive ion. The process of the reaction of all heterocyclic compounds were observed which the LUMO energy changed to a more stable level or a more negative value and the HOMO energy shifted to a less stable level, or a less negative value. The HOMO & LUMO energy levels display the ability of the electron donor and receptor, respectively, where the less stable HOMO energy level performs as a good electron donor. Conversely, the more stable LUMO energy level performs as a good electron receptor.

Thus, the reaction of three heterocyclic compounds produce the three complexes ($C_{58}BN$/**1**/$C_{58}BN$, $C_{58}BN$/**2**/$C_{58}BN$ and $C_{58}BN$/**3**/$C_{58}BN$) which take the role of the better electron donors and receptors. We then consider the different abilities of the electron donor and receptor of each heterocyclic compound which illustrate that all of the complexes exhibit a rather similar ability of the electron donor and receptor except for the $C_{58}BN$/**2/**$C_{58}BN$ complex where the 3,8-Phenanthroline heterocyclic compound exhibits less ability as an electron receptor due to the less stable LUMO energy level being about -4.89 eV. In addition, the calculated binding energy of the three complexes are not significantly different (52.32, 55.05 and 56.69 kcal/mol), which have the same logic for the mono fullerene complexes as for the nucleophilities or basicities of each nucleophile which are not significantly different.

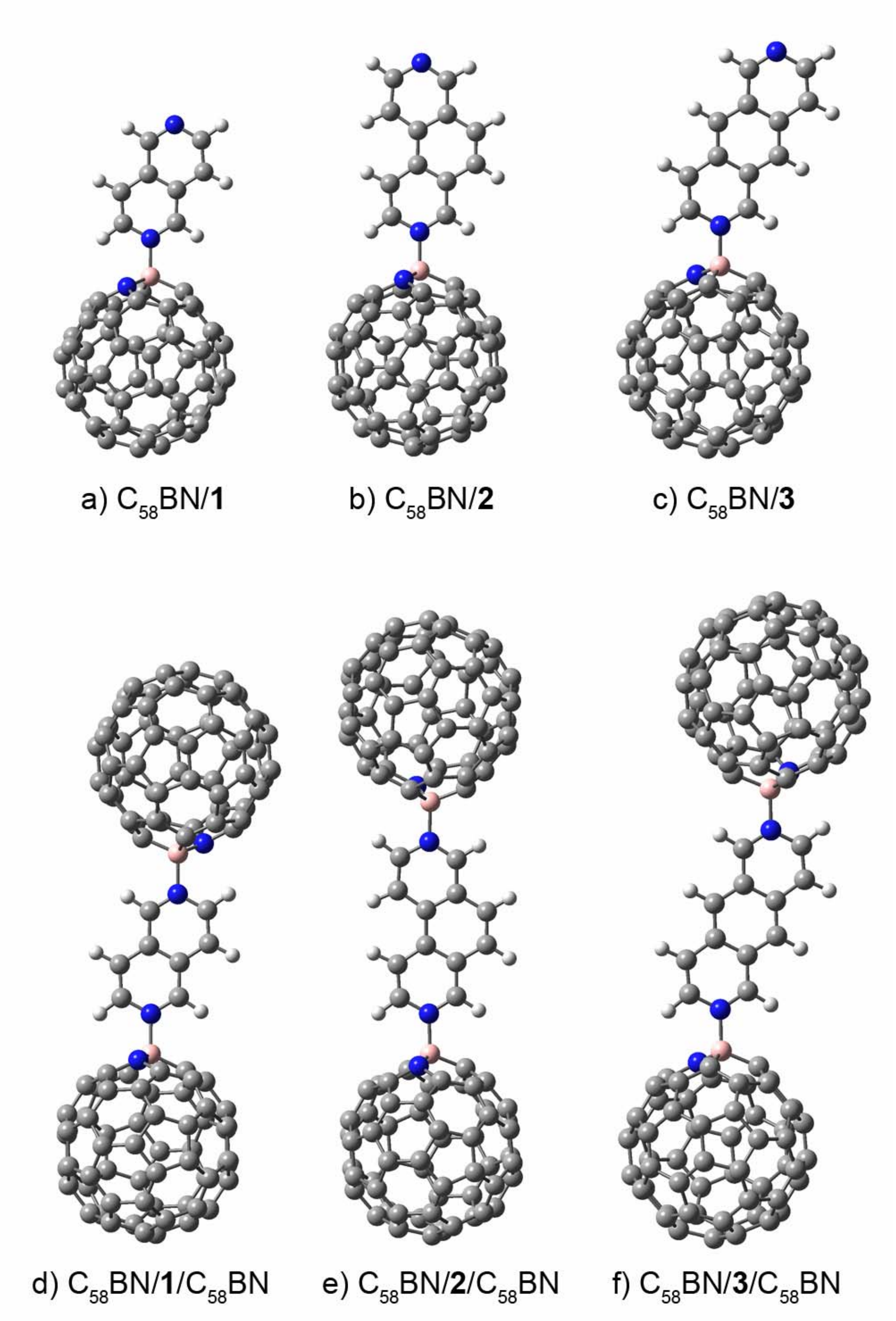
2. Isolated heterocyclic compounds and their interplay to BN-doped fullerene

As for the isolated heterocyclic compounds, the calculated energy gaps for the 2,6-diazanaphthalene, 3,8-diazaphenanthrene and 2,6-diazaanthracene compounds are 2.97, 3.22 and 2.30 eV, respectively. From the chemical point of view, the electronic conductivities for all compounds are in the order of 2,6-diazaanthracene > 2,6-diazanaphthalene > 3,8-diazaphenanthrene.

Additions of the heterocyclic compounds to the BN-doped fullerene show drastically enhancement of the electronic conductivity which is presented by the significant destabilization on the HOMO level resulting in the reduction of energy gaps by 1.03, 0.82 and 1.23 eV for $C_{58}BN$/**1**, $C_{58}BN$/**2** and $C_{58}BN$/**3**, respectively. Furthermore, the corresponding calculated binding energies are 28.82, 29.95 and 30.42 kcal/mol which suggests strong communications between $C_{58}BN$ and heterocyclic compounds. As a result, obviously, the electronic transportation between two BN-doped fullerene units might be improved via the bridging heterocyclic compounds.

3. The interconnection BN-doped fullerene dimer via heterocyclic compound

Fig. 22 shows BN-doped fullerene dimer interconnection via the linkage heterocyclic compounds. The energy gaps are significantly reproduced which give the values of 0.10, 0.23 and ~0.00 eV for $C_{58}BN$/**1**/$C_{58}BN$, $C_{58}BN$/**2**/$C_{58}BN$ and $C_{58}BN$/**3**/$C_{58}BN$, respectively, These promoted the superior electronic communications between the two BN-doped fullerene cages via bridging compounds. Likewise, there was more stabilization among the BN-doped fullerene dimer and the intermolecular bridging compounds as shown by the exothermic binding energies of 52.32, 55.05 and 56.69 kcal/mol for $C_{58}BN$/**1**/$C_{58}BN$, $C_{58}BN$/**2**/$C_{58}BN$ and $C_{58}BN$/**3**/$C_{58}BN$, respectively. In all cases, the 2,6-diazaanthracene ($C_{12}H_8N_2$, **3**) molecule is predicted to be the most preferable molecular bridging between the BN-doped fullerene dimer.

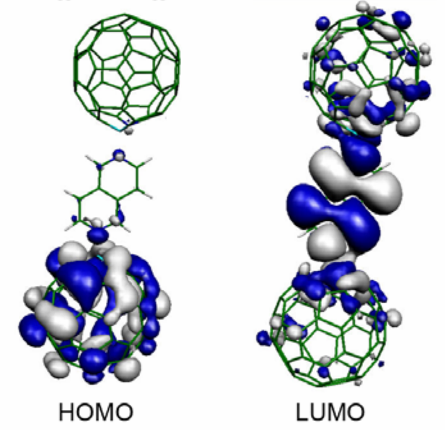


a) $C_{58}BN$/**1** b) $C_{58}BN$/**2** c) $C_{58}BN$/**3**

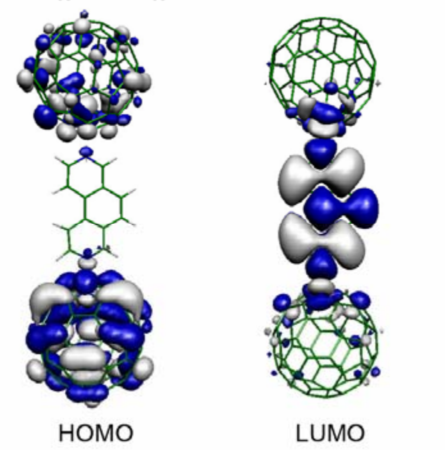
d) $C_{58}BN$/**1**/$C_{58}BN$ e) $C_{58}BN$/**2**/$C_{58}BN$ f) $C_{58}BN$/**3**/$C_{58}BN$

Figure 22 Illustrations of mono- and di-C_{60} complexes with 2,6-diazanaphthalene (**1**),3,8-diazaphenanthrene (**2**) and 2,6-diazaanthracene (**3**).

(a) $C_{58}BN$/**1**/$C_{58}BN$



(b) $C_{58}BN$/**2**/$C_{58}BN$



(c) $C_{58}BN$/**3**/$C_{58}BN$

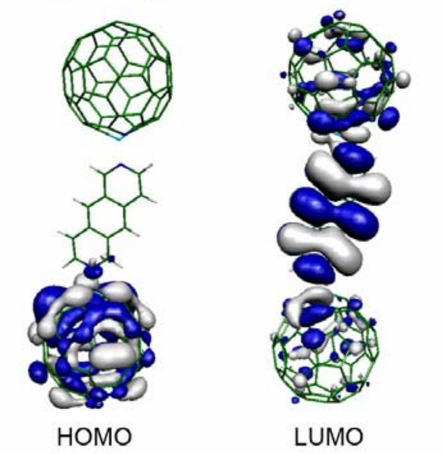


Figure 23 Molecular orbitals contour plots for $C_{58}BN$/**1**/$C_{58}BN$, $C_{58}BN$/**2**/$C_{58}BN$ and $C_{58}BN$/**3**/$C_{58}BN$ systems

Fig. 23 shows the molecular orbitals (MOs) contour plots for HOMO and LUMO for $C_{58}BN$/**1**/$C_{58}BN$, $C_{58}BN$/**2**/$C_{58}BN$ and $C_{58}BN$/**3**/$C_{58}BN$ systems. As for $C_{58}BN$/**1**/$C_{58}BN$ and $C_{58}BN$/**3**/$C_{58}BN$, the similarities of the contour features are clearly seen. The major contributions of HOMOs are that they are mainly dominant by the BN-doped fullerene (~96%) while the LUMOs are mostly lead by heterocyclic compounds (~88%) with non negligible contributions from BN-doped fullerene (~6%). As for the $C_{58}BN$/**2**/$C_{58}BN$ system, the HOMO contributions are possessed by both BN-doped fullerene centers with a non equivalent extent (~54% vs 45%). The LUMO shows the major contributions hold for **3**.

Table 5 Molecular orbital contributions.

Systems	**Electron contributions (%)**			
	HOMO - 1	**HOMO**	**LUMO**	**LUMO + 1**
$C_{58}BN$/**1**/$C_{58}BN$				
$C_{58}BN$	94.22	1.73	6.43	3.71
1	4.59	2.54	88.06	91.75
$C_{58}BN$	1.19	95.73	5.51	4.54
$C_{58}BN$/**2**/$C_{58}BN$				
$C_{58}BN$	44.02	53.53	3.40	1.09
2	3.01	1.14	93.36	98.25
$C_{58}BN$	52.97	45.34	3.25	0.66
$C_{58}BN$/**3**/$C_{58}BN$				
$C_{58}BN$	94.92	0.12	6.56	75.81
3	4.93	2.59	88.90	21.99
$C_{58}BN$	0.14	97.29	4.55	2.19

CONCLUSIONS

We have carried out quantum chemical calculations to study the electronic property of the BN-doped carbon nanomaterials grafted with N-nucleophiles. The PBE density functional theory (DFT) method with the def-SV(P) basis set and RI approximation implemented in the TURBOMOLE code was used. The degree of grafting the BN-doped SWCNT with N-nucleophiles (*R-group*) wase reported in term of binding energy (E_b). The relative of binding energy is directly proportional to the pK_a value of N-nucleophiles. The charge redistribution derived from Natural Population Analysis (NPA) shows that the charge transfer can be found when the BN-doped SWCNT was grafted with m-nitroaniline and pyridine. The BN-doped SWCNT acts as an electron acceptor and gains electron from the grafting N-nucleophiles. The energy gap of the BN-doped SWCNT grafted with m-nitroaniline and pyridine decreases by about 0.25 and 0.35 eV, respectively, compared to that of the isolated BN-doped SWCNT of 0.43 eV. The partial density of states analysis indicated that the total density of states at the Fermi level increases when the BN-doped SWCNT was grafted with m-nitroaniline and pyridine. This results in the improvement of the conductivity of materials.

The grafting of BN-doped C_{60} with 2,6-diazanapthalene (**1**), 3,8-diazaphenanthene (**2**), and 2,6-diazaantracene (**3**) greatly reduced the energy gaps by 1.03, 0.82 and 1.23 eV, respectively, as compared to the isolated C_{60}. The electronic communication between two BN-doped fullerene molecules was drastically improved when they were linked through these heterocyclic N-nucleophiles. The corresponding energy gap reduces by 1.54, 1.41 and 1.64 eV for C_{58}BN/**1**/C_{58}BN, C_{58}BN/**2**/C_{58}BN and C_{58}BN/**3**/C_{58}BN, respectively, compared to the isolated C_{60}. Likewise, the binding energies of such complexes are exothermic by 23.50, 25.10 and 26.27 kcal/mol. These quite high exothermic energies suggest that the bridging dimer formations are thermodynamically favorable.

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CURRICULUM VITAE

NAME : Mr. Norawit Krainara

BIRTH DATE : November 25, 1981.

BIRTH PLACE : Nakornsrithammarat, Thailand

EDUCATION :

YEAR	**INSTITUTION**	**DEGREE/DIPLOMA**
2004	Prince of songkla Univ.	B.S. (Chemistry)

SCHOLASHIP : Development and Promotion of Science and Technology Talents Project (2001-2005)

PUBLICATION

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PRESENTATION

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