

Conduction Properties of BN-doped Fullerene Chain obtained by Density Functional Theory Calculations

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ABSTRACT

We investigated the systematic DFT studies on the electronic properties of the bridging of BN-doped fullerene ($C_{58}BN$) dimer. The BN substitution into the C_{60} framework reduces the HOMO-LUMO energy gap by ~ 0.2 eV. The addition of heterocyclic molecules, namely, 2,6-Naphthyridine, 3,8-Phenanthroline and 2,6-Diazaanthracene connecting two $C_{58}BN$ s greatly destabilize the HOMO and reduce the energy gap. The energy gaps, compared to C_{60} , for 2,6-Naphthyridine, 3,8-Phenanthroline and 2,6-Diazaanthracene complex systems are greatly reduced by 1.54, 1.41 and 1.64 eV, respectively. The corresponding binding energies of such complexes have an exothermicity of 52.3, 55.0 and 56.7 kcal/mol, respectively. These high exothermic energies suggest that the bridging dimer formations are thermodynamically favorable and that the conductivity of the BN-doped fullerene is significantly improved by these formations of the bridging dimer.

Keywords: BN-doped Fullerene, C_{60} dimer, Conduction Properties, DFT

1 INTRODUCTION

The electronic properties of several fullerene derivatives have attracted considerable research interest due to their various properties [1]. For instance, the bisfullerene compound, consisting of two interacting fullerene centers, is of high interest for the electronic communication between two C_{60} active centers, has implications for optical and electronic applications. Several efforts have been devoted to exploring such electronic communication by introducing various linkage species between two C_{60} centers (see refs. [2-6] for examples). Metal cluster bridging two fullerenes exhibits remarkable electronic interaction between the two C_{60} [2]. However, it was found that no electronic communication has been observed for the

organic-based bisfullerenes in which linkage species is longer than a single atom [3-6]. The modifications of the fullerene structure in which some carbons are replaced by heteroatoms, referred to as heterofullerenes [7], have also been introduced. Azaborafullerenes ($C_{58}BN$) have received most computational attention. The $C_{58}BN$ system is isoelectronic to the C_{60} fullerene. It has been found that the BN heteroatoms play a vital role in the electronic property improvement by reducing the energy gap by ~ 0.2 eV [8,9] compared to the fullerene system. Moreover, Chen *et al.* [1] found that $C_{58}BN$ is slightly more aromatic than C_{60} . Therefore, the presence of BN in fullerene centers might help to promote electronic communication between two fullerene cages through appropriate linkage compounds.

In this study, we propose the possibilities to modify the electronic communication between two BN-doped fullerene ($C_{58}BN$) frameworks with bridging heterocyclic compounds.

2 METHODOLOGY

2.1 System descriptions

Fullerene (C_{60}) and BN-doped fullerene ($C_{58}BN$) were selected as reference systems, as illustrated in Fig. 1. As for the BN-doped fullerene, the C-C bond connecting two hexagonal structures were substituted by BN heteroatoms since it has been reported to be the most stable structure among their isomers [10-12]. Three types of heterocyclic compounds, namely, 2,6-Naphthyridine ($C_8H_6N_2$, **1**), 3,8-Phenanthroline ($C_{12}H_8N_2$, **2**) and 2,6-Diazaanthracene ($C_{12}H_8N_2$, **3**) were selected to study the modified interfullerene electronic conductivity (see Figs. 1c-e). Such bridging compounds were interacted directly to the 'boron atom' in the $C_{58}BN$ structure because of its high electron acceptor efficiency. Likewise, two $C_{58}BN$ active centers were connected together by heterocyclic compounds which were interconnected at the boron positions of each $C_{58}BN$ ball.

3 RESULTS AND DISCUSSION

3.1 Fullerene and BN-doped fullerene as reference systems

The C_{60} fullerene has the average bond distances of 1.41 and 1.46 Å, for the C-C connecting hexagonal-hexagonal and hexagonal-pentagonal, respectively. The BN heteroatoms induce the local structural distortion around the BN substituted site. The B-N, B-C and N-C bond distances are 1.45, 1.55 and 1.42 Å, respectively, resulting in the upward shift of B atoms from the original position of C analogue. Our results are in good agreement with the literatures [8].

The HOMO-LUMO energy gap obtained for fullerene was calculated to be 1.64 eV. An addition of BN heteroatoms into fullerene reduced the corresponding energy gap to 1.46 eV, which indicated an improvement for the electronic conductivity properties, although it was found to be a rather small alteration. The reduction of energy gaps were in good agreement with literatures which indicated that the substitution of BN atoms to fullerene slightly reduced the energy gap ~0.2 eV [8,9].

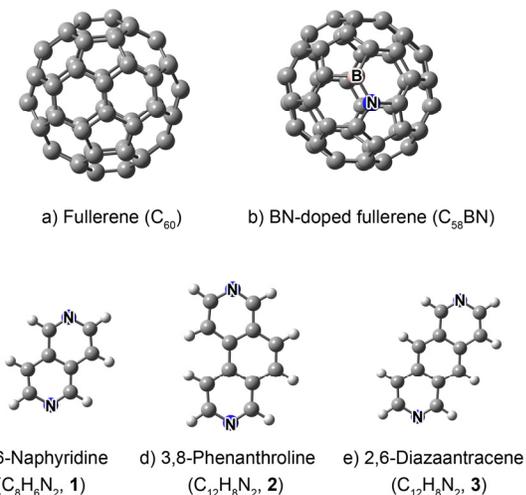


Figure 1: Illustrations of a) Fullerene (C_{60}), b) BN-doped fullerene ($C_{58}BN$), c) 2,6-Naphthyridine ($C_8H_6N_2$, **1**), d) 3,8-Phenanthroline ($C_{12}H_8N_2$, **2**) and e) 2,6-Diazaanthracene ($C_{12}H_8N_2$, **3**) structures.

2.2 Electronic structure calculations

Full geometry optimization of such systems has been carried out by means of density functional theory (DFT) using the PBE exchange-correlation functional [13] implemented in TURBOMOLE code [14]. The standard split-valence polarization SV(P) (double- ζ with polarization) basis sets with (7s4p1d)/[3s2p1d] contraction [15] were used for all atoms in the system. It is noted here that we did not take into consideration the underestimation of energy gaps obtained from PBE calculations since we were mainly interested in the trend observed for the electronic conductivity improvements of the connection of fullerene dimer by the spacer linkage heterocyclic compounds. We also investigated some selected systems using B3LYP/6-31G* level of theory and found that the relative energy gap alterations due to the effects of either BN doped into fullerene or the spacer linkage heterocyclic compounds are in the same order as reported in our PBE calculations (B3LYP/6-31G*: Relative energy gap reductions of $C_{58}BN$, $C_{58}BN/1$, $C_{58}BN/2$ and $C_{58}BN/3$, compared to C_{60} , are 0.22, 1.01, 0.82 and 1.28, respectively).

The energy gaps between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) were calculated to evaluate the electronic conductivity of bisfullerene complexes. Moreover, the HOMO and LUMO contour plots for selected systems were also demonstrated to clarify how electronic properties of systems alter as a result of bridging heterocyclic compounds.

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

Table 1: Relative energy gap reductions of systems studied compared to C_{60} ($E_{gap} = 1.64$ eV).

3.2 Isolated heterocyclic compounds and their interplay to BN-doped fullerene

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

Additions of the heterocyclic compounds to the BN-doped fullerene show drastic enhancement of the electronic conductivity which is presented by the great 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 suggest the strong interactions between $C_{58}BN$ and heterocyclic compounds. The bond distances of B-N and B-C of the $C_{58}BN$ are elongated from 1.45 to 1.55 Å and 1.55 to 1.61 Å, respectively while N-C bond distances are not significantly changed. As a result, the B atom moves upward farther from the fullerene surface when it interacts with the heterocyclic compounds. The improvement of the electronic transportation in the systems could be explained by the electronic alteration of the B atom from sp^2 toward sp^3 hybridization.

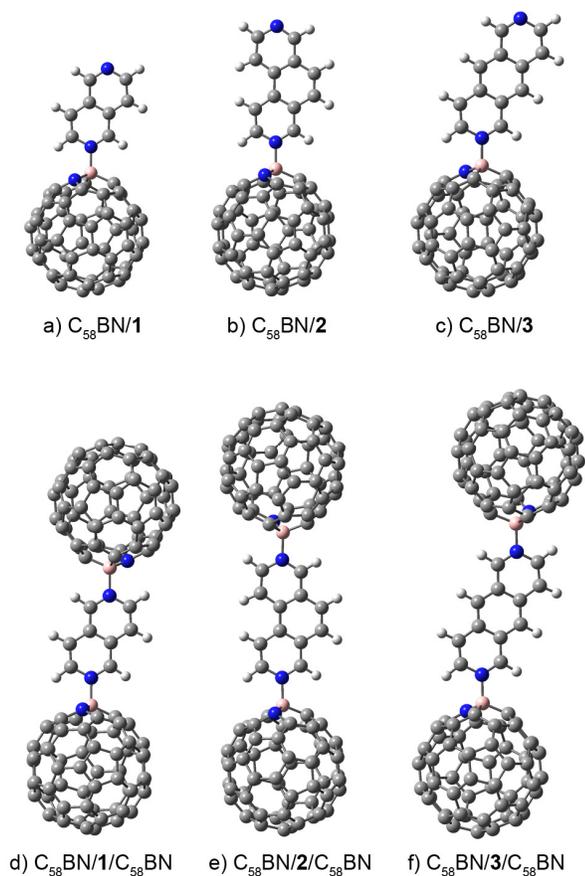


Figure 2: Illustrations of a) $C_{58}BN/1$, b) $C_{58}BN/2$ and c) $C_{58}BN/3$, d) $C_{58}BN/1/C_{58}BN$, e) $C_{58}BN/2/C_{58}BN$ and f) $C_{58}BN/3/C_{58}BN$ structures.

3.3 The interconnection of BN-doped fullerene dimer via heterocyclic compound

Fig. 2 shows BN-doped fullerene dimer interconnection via the linkage heterocyclic compounds. The energy gaps are drastically reduced to 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, which promoted the superior electronic communications between two bridging BN-doped fullerene cages. The formation of the bridging

BN-doped fullerene dimer has 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. The $C_{58}BN/3/C_{58}BN$ is predicted to be the most stable complex and has the most electronic interaction.

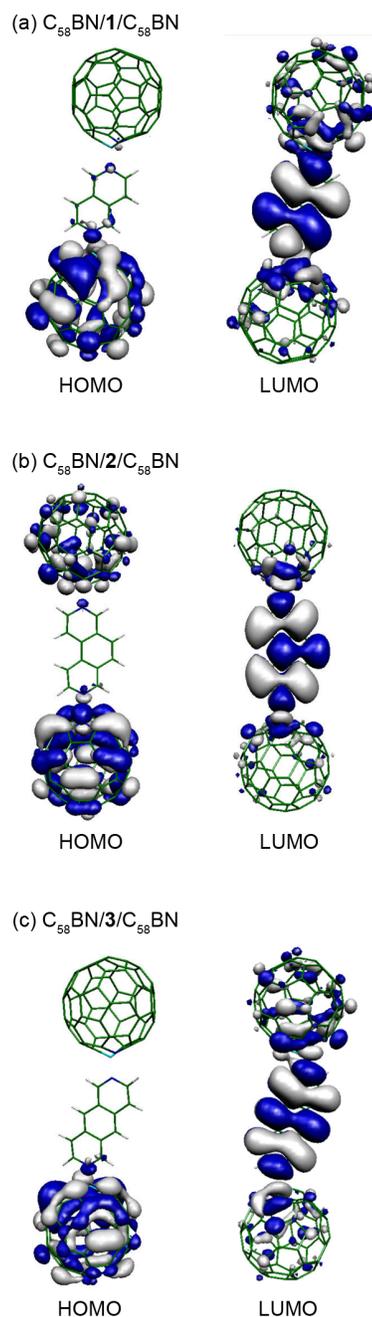


Figure 3: MOs contour plots for $C_{58}BN/1/C_{58}BN$, $C_{58}BN/2/C_{58}BN$ and $C_{58}BN/3/C_{58}BN$ systems.

Fig. 3 shows the molecular orbital (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 contour features are clearly seen. The major contributions of HOMOs are mainly dominant by the BN-doped fullerene (~96%) while the LUMOs are mostly leading by bridging heterocyclic compounds (~88%) with the non negligible contributions from two BN-doped fullerenes (~12%). As for the $C_{58}BN/2/C_{58}BN$ system, the HOMO contributions are almost exclusively from the two BN-doped fullerene centers with a non equivalent extent (~54% vs 45%). The LUMO shows the most contributions from the bridging heterocyclic compounds (93%) and a little contribution (~7%) from the two BN-doped fullerenes.

These molecular orbital contour plots suggest that the electronic communication between the bridging species and the BN-doped fullerenes is in the opposite direction as in the Rh_6 -bisfullerene complex reported by Lee *et al.* [2]. In the Rh_6 cluster bridging bisfullerene, the electronic communication is originated from the occupied molecular orbitals of the metal cluster to the unoccupied molecular orbital of the fullerene. Whereas, in this study, the electronic communication would flow from the occupied molecular orbitals of the BN-doped fullerene to the unoccupied molecular orbitals of the bridging heterocyclic compounds.

4 CONCLUSIONS

We have carried out quantum calculations on the basis of the density functional theory (PBE) method with the def-SV(P) basis set using the TURBOMOLE code. The substitution of BN moieties onto the C_{60} slightly reduces the HOMO-LUMO energy gap by ~0.2 eV (see Table 1). The addition of the 2,6-Naphthyridine, 3,8-Phenanthroline and 2,6-Diazaanthracene compounds on the BN-doped C_{60} greatly destabilizes the HOMO and reduces the energy gaps by 1.03, 0.82 and 1.23 eV, respectively. The electronic communications between two BN-doped fullerene improve drastically when the bridging dimers are formed, which greatly reduce the corresponding energy gaps 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. Likewise, the binding energies of such complexes have exothermicities of 52.3, 55.0 and 56.7 kcal/mol. These high exothermic energies suggest that the bridging dimer formations are thermodynamically favorable. The conductivities of the BN-doped fullerene dimer are drastically improved by the formations via the bridging heterocyclic compounds.

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