

# Tailorable acceptor $C_{60-n}B_n$ and donor $C_{60-m}N_m$ pairs for molecular electronics

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Our first-principles calculations demonstrate that  $C_{60-n}B_n$  and  $C_{60-m}N_m$  molecules can be engineered as the acceptors and donors, respectively, which are needed for molecular electronics, by properly controlling the dopant number  $n$  and  $m$  in  $C_{60}$ . As an example, we show that acceptor  $C_{48}B_{12}$  and donor  $C_{48}N_{12}$  are promising components for molecular rectifiers, carbon nanotube-based  $n$ - $p$ - $n$  ( $p$ - $n$ - $p$ ) transistors and  $p$ - $n$  junctions.

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Modern microelectronics and computation are advancing at an extremely fast rate because of remarkable circuit miniaturization [1]. However, this trend will soon reach the scale of atoms or molecules. To continue toward faster and smaller computers, new schemes are required. Molecular electronics [2] is one such approach.

One major problem in molecular electronics is connecting the functional molecules and assigning the observed electrical properties in an unambiguous way to the molecules in question [3,4]. Fullerenes [5] are large enough to be identified by transmission electron microscopy or scanning probe methods [4], are stable and easy to build into molecular circuits [5,6], and might be inserted into single-walled carbon nanotubes (SWNT) [7]. Hence, fullerenes should be ideal components for molecular electronics.

As in semiconductor electronics [1], acceptor/donor pairs are critical for use in molecular electronics, for example, molecular rectifiers [2], nanoscale  $p$ - $n$ - $p$  transistors and  $p$ - $n$  junctions [8]. For traditional silicon doping, group V atoms (for example, phosphorous) act as donors and group III (for example, boron) are acceptors. Analogous acceptor/donor schemes are needed in molecular electronics [2]. Fullerenes are unique because they can be doped in several different ways (for example, endohedral [5], substitutional [5,9–11] and exohedral doping [5]). This should provide a wide range of possible acceptor/donor schemes.

To design active molecular devices, components with controllable electronic properties are needed [2,3]. For example, to obtain molecular rectification, the lowest unoccupied molecular orbital (LUMO) of the acceptor should lie at or slightly above the Fermi level of the electrode and above the highest occupied molecular orbital (HOMO) of the donor [2]. Hence it is important to search for desired acceptor/donor pairs which satisfy the requirement. In this letter, we suggest a controlled approach to obtain such pairs from  $C_{60}$  molecules by using substitutional doping. Because the average carbon-carbon bond length in  $C_{60}$  is slightly larger than that in graphite, which can only be substitutionally doped by boron, and the force

constants [5] are somewhat weakened by the curvature of the  $C_{60}$  surface, both boron and nitrogen can substitute for one or more carbons in  $C_{60}$  [9–11]. Our first-principles calculations demonstrate that  $C_{60-n}B_n$  and  $C_{60-m}N_m$  molecules can be engineered as the acceptors and donors, respectively, which are desired for molecular electronics by properly controlling the dopant number  $n$  and  $m$ . As an example, we present the electronic properties of the acceptor  $C_{48}B_{12}$  and donor  $C_{48}N_{12}$ , and discuss their potential applications in molecular electronics.

First, we discuss the electronic properties of  $C_{60-n}B_n$ ,  $C_{60-n}N_n$  and  $C_{60}$  to show that  $C_{60-n}B_n$  and  $C_{60-n}N_n$  can act as controlled dopants. The number  $n$  ranges from 1 to 12. Since there are many isomers [12] of  $C_{60-n}X_n$  at fixed  $n$ , we only take the dopant assignment of Hultman *et al.* [11] as an example [13]: each pentagon receives a maximum of one dopant X, and two X are separated from each other by two carbon atoms. The optimized geometry and total energy are calculated by using the Gaussian 98 program [14,15] with the B3LYP [16] hybrid density functional theory (DFT) [17] and 6-31G(d) basis set. The calculated results are summarized in Table I. It is found that the binding energy of  $C_{60-n}X_n$  ( $X=B,N$ ) decreases monotonically with increasing integer  $n$ . For  $C_{60-n}B_n$ , the binding energy is 0.21 eV/atom to 0.38 eV/atom lower than that ( $E_b = 6.98$  eV/atom) of  $C_{60}$ . For  $C_{60-n}N_n$ , it is 0.10 eV/atom to 0.61 eV/atom lower than that of  $C_{60}$ . The stabilities of  $C_{60-n}B_n$  and  $C_{60-n}N_n$  are comparable to but less than that of  $C_{60}$ . In 1991, Smalley and coworkers [9] successfully synthesized  $C_{60-n}B_n$  with  $1 \leq n \leq 6$ . In 1995, Hummelen *et al.* [10] produced  $C_{59}N$ . Very recently, Hultman *et al.* [11] have reported the existence of  $C_{48}N_{12}$ . These experiments show that certain stable  $C_{60-n}X_n$  ( $X=B,N$ ) can be made. Our results show that other B- or N-doped  $C_{60-n}X_n$  structures for  $n \leq 12$  have similar stability. Our calculated ionization potential ( $E_I = 7.32$  eV) and electron affinity ( $E_A = 2.40$  eV) for  $C_{60}$  agree well with experiments ( $E_I = 7.54 \pm 0.01$  eV [18] and  $E_A = 2.689 \pm 0.008$  eV [19]), indicating the accuracy of our calculations for  $C_{60-n}X_n$ . Among  $C_{60}$  and  $C_{60-n}X_n$

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(X=B,N) at fixed  $n$ ,  $C_{60-n}B_n$  has the highest electron affinity, while  $C_{60-n}N_n$  has the lowest ionization potential, indicating that  $C_{60-n}B_n$  and  $C_{60-n}N_n$  can serve as electron acceptor and donor, respectively.

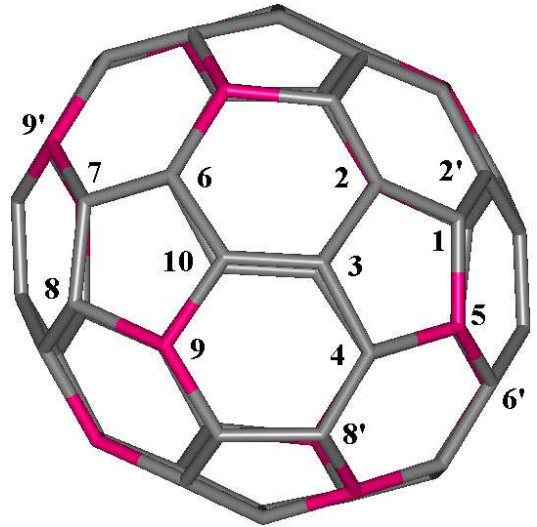
Calculations of LUMO and HOMO energies are necessary to explore combinations of donors and acceptors suitable for molecular electronics. Table I shows the change of the LUMO/HOMO energies (and LUMO-HOMO gaps  $E_g = E_l - E_h$ ) as we vary the dopant number  $n$  in the  $C_{60-n}X_n$  molecule. Hence, acceptor/donor pairs which satisfy the required conditions in molecular electronics can be obtained by controlling the dopant number  $n$  and  $m$  in  $C_{60-n}B_n$  and  $C_{60-m}N_m$ . For example, based on the acceptor LUMO and donor HOMO shown in Table I, we may choose acceptor/donor pairs, such as  $C_{58}B_2/C_{58}N_2$ ,  $C_{54}B_6/C_{54}N_6$ ,  $C_{49}B_{11}/C_{51}N_9$ , or  $C_{48}B_{12}/C_{48}N_{12}$  to build molecular rectifiers exhibiting similar rectification behaviors. In the following, we take  $C_{48}B_{12}/C_{48}N_{12}$  as one example to show their applications in molecular electronics.

**Table I:** LUMO ( $E_l$ , in eV), HOMO ( $E_h$ , in eV), binding energy ( $E_b$ , in eV/atom), ionization potential ( $E_I$ , in eV), and electron affinity ( $E_A$ , in eV) calculated for  $C_{60-n}X_n$  (X=B,N) using B3LYP/6-31G(d).

n	$C_{60-n}B_n$					$C_{60-n}N_n$				
	$E_l$	$E_h$	$E_b$	$E_I$	$E_A$	$E_l$	$E_h$	$E_b$	$E_I$	$E_A$
1	-4.26	-5.57	6.77	6.77	3.07	-3.63	-4.72	6.88	5.93	2.15
2	-4.64	-5.25	6.75	6.35	3.53	-3.71	-4.64	6.82	5.85	2.27
3	-4.21	-5.49	6.74	6.37	3.32	-3.72	-4.69	6.78	5.92	2.29
4	-4.43	-5.60	6.73	6.79	3.32	-3.91	-4.56	6.73	5.83	2.19
5	-4.59	-5.54	6.71	6.85	3.56	-3.74	-4.56	6.69	5.95	2.20
6	-4.55	-5.49	6.70	7.01	2.98	-3.74	-4.61	6.64	5.85	2.32
7	-4.49	-5.54	6.67	6.75	3.23	-3.58	-4.59	6.60	5.91	2.39
8	-4.62	-5.34	6.66	6.44	3.50	-3.60	-4.41	6.55	5.65	2.36
9	-4.65	-5.43	6.64	6.61	3.34	-3.49	-4.45	6.51	5.77	1.90
10	-4.57	-5.44	6.63	6.57	3.45	-3.31	-4.28	6.46	5.52	1.89
11	-4.45	-5.61	6.62	6.87	3.30	-3.36	-4.35	6.41	5.71	2.29
12	-4.24	-5.58	6.60	6.73	3.08	-2.61	-4.38	6.37	5.66	1.49

The molecular geometry (size) and symmetry play important roles in molecular electronics [2,3]. For example, an important factor in inducing rectification is some geometric asymmetry in the molecular junction [3].  $C_{60}$  is a truncated icosahedron with a perfect  $I_h$  symmetry. Then, the changes in geometry (size) and symmetry of  $C_{60-n}X_n$ , due to the dopant-induced effects, are needed to know. Fig.1 shows the optimized structure of  $C_{48}B_{12}$ . For comparison, similar calculations were done for  $C_{60}$  and  $C_{48}N_{12}$ . The equilibrium  $C_{48}B_{12}$ , similar to  $C_{48}N_{12}$  [11], has one dopant (boron) per pentagon and two dopants (boron) preferentially sit in a hexagon. In  $C_{48}X_{12}$  (X=B, N), the doping-induced distortion from the perfect  $C_{60}$  sphere is not localized to the neighborhood of each dopant but extends throughout the whole

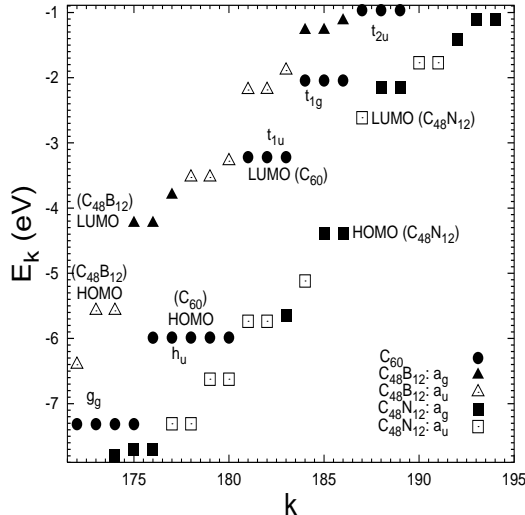
cage. The symmetry of  $C_{48}B_{12}$  is the  $C_i$  point group, different from the  $S_6$  symmetry for  $C_{48}N_{12}$  [11]. This is due to their opposite electronic polarization, as discussed below. The molecular structure is examined by calculating the average distances (or radii R) from each atom to the center of the molecule.  $C_{48}B_{12}$  has an ellipsoidal structure, as in  $C_{48}N_{12}$ , with 10 unique sites labelled 1 to 10 in Fig.1 and 10 different radii ranging from 0.347 nm (site 2, 2') to 0.387 nm (site 8, 8'). In contrast, the 10 unique radii for  $C_{48}N_{12}$  range from 0.340 nm (site 7) to 0.362 nm (site 5). For  $C_{60}$ , each carbon atom has an equal radius  $R = 0.355$  nm, the same as that found in experiment [20]. Furthermore, we find 15 unique bonds (specified in Fig.1) in  $C_{48}B_{12}$ : 6 boron-carbon bonds with lengths between 0.154 nm and 0.159 nm, and 9 carbon-carbon bonds with 0.139 nm to 0.150 nm lengths. In comparison,  $C_{48}N_{12}$  has 6 nitrogen-carbon bonds with lengths ranging from 0.141 nm to 0.143 nm, and 9 carbon-carbon bonds with lengths from 0.139 nm to 0.145 nm.  $C_{60}$ , however, has one kind of single C-C bond (0.145 nm) and one kind of double C=C bond (0.139 nm), which are in excellent agreement with experiments (0.14459 nm and 0.13997 nm [20]).



**FIG. 1:**  $C_{48}B_{12}$  structure optimized with B3LYP/6-31G(d). Red (grey) is for B (C) sites. The 15 bonds between labeled vertices are all unique.

To determine the electronic polarization, Mulliken charge analysis [21] was performed for the on-site charge  $Q_m$  of atoms in  $C_{48}B_{12}$ ,  $C_{48}N_{12}$  and  $C_{60}$ .  $C_{48}B_{12}$  has two types of boron dopants: one boron with net Mulliken charge  $Q_m = 0.164 |e|$  (site 5) and one with  $Q_m = 0.187 |e|$  (site 9), while carbon atoms in  $C_{48}B_{12}$  have negative  $Q_m$  in the range from  $-0.004 |e|$  (site 3) to  $-0.083 |e|$  (site 8). In  $C_{48}N_{12}$ , there are two types of nitrogen dopants: one nitrogen with  $Q_m = -0.595 |e|$  (site 5) and one with  $Q_m = -0.600 |e|$  (site 9), and two types of carbon atoms: one-fourth of the carbon atoms with negative  $Q_m$  ( $-0.0125 |e|$  at site 2 and  $-0.0298 |e|$  at site 3) and three-fourths of the carbon atoms with  $Q_m$  in the

range of  $0.192 |e|$  (site 6) to  $0.227 |e|$  (site 4). In  $C_{60}$ ,  $Q_m = 0$  for each carbon atom. Although the Mulliken analysis cannot estimate the atomic charges quantitatively, their signs are correct [21]. Hence,  $C_{60}$  is isotropic, while  $C_{48}B_{12}$  and  $C_{48}N_{12}$  have opposite electronic polarizations, leading to their different symmetries.



**FIG. 2.:** Orbital energies  $E_k$  and symmetries of the  $k$ th eigenstate for  $C_{48}X_{12}$  ( $X=B,C,N$ ) calculated with B3LYP/6-31G(d).

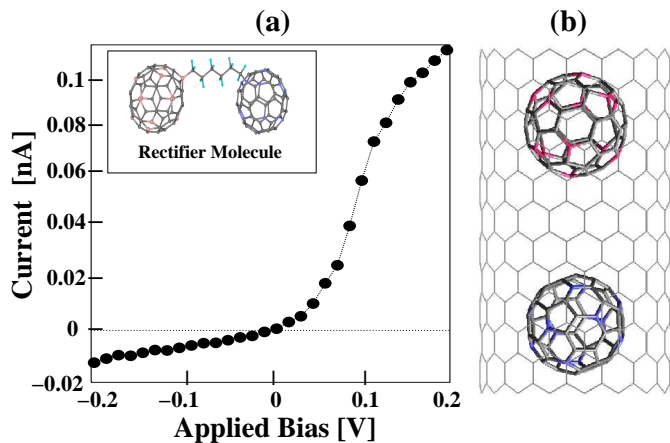
Applications of acceptors  $C_{60-n}B_n$  and donors  $C_{60-n}N_n$  require the proper line-up of energy levels. Upon boron or nitrogen doping, the degeneracy of the original  $C_{60}$  levels, shown in Fig.2, is removed by the structural distortion of the icosahedral symmetry.  $C_{48}B_{12}$  ( $C_{48}N_{12}$ ) is isoelectronic with  $C_{60}^{+12}$  ( $C_{60}^{-12}$ ). Replacing 12 carbon atoms by 12 boron atoms results in removing 10 electrons from the HOMO ( $h_u$  symmetry,  $E_h = -5.99$  eV) of  $C_{60}$  and 2 electrons from the 2nd HOMO ( $g_g$  symmetry) of  $C_{60}$ . In contrast, replacing 12 carbon atoms by 12 nitrogen atoms leads to a complete filling of 6 electrons in the LUMO ( $t_{1u}$  symmetry,  $E_l = -3.22$  eV) of  $C_{60}$  and 6 electrons in the 2nd LUMO ( $t_{1g}$  symmetry) of  $C_{60}$ . Quantitatively, Fig.2 shows the orbital energies of  $C_{48}B_{12}$  and  $C_{48}N_{12}$ . They are different from each other because of the difference in valency of B and N atoms. For  $C_{48}N_{12}$ , the HOMO is a doubly-degenerate level of  $a_g$  symmetry, while the LUMO is a non-degenerate level with  $a_u$  symmetry. For  $C_{48}B_{12}$ , the HOMO and LUMO are doubly-degenerate levels of  $a_u$  and  $a_g$  symmetries, respectively. These calculations show that  $C_{48}B_{12}$ 's LUMO is just above  $C_{48}N_{12}$ 's HOMO and the approximate potential difference is about 1.63 eV. Thus, both  $C_{48}B_{12}$  and  $C_{48}N_{12}$  have precisely the properties required for a proper rectifier behavior as will be demonstrated below.

Various experiments [22] have shown that individual molecules can act as molecular rectifiers [2]. The inset in Fig.3(a) shows a rectifier molecule consisting of a donor

$C_{48}N_{12}$  and an acceptor  $C_{48}B_{12}$  connected by a tunneling bridge (a  $\sigma$ -electron system,  $-(CH_2)_6-$ ). The bridge forms a potential barrier that isolates the donor from the acceptor on the time-scale of electron motion to or from the electrodes [2] (see review [6] about synthesis techniques which have successfully bridged  $C_{60}$  dimers through electroactive spacers). Following the Aviram-Ratner scheme [2], we expect that electron current would pass from the cathode to the anode via acceptor, bridge and donor. Since  $C_{48}B_{12}$ 's LUMO is -4.2 eV, we may choose metallic carbon nanotubes (work function  $\phi \approx 5$  eV [23]), gold, silver or copper ( $\phi \approx 4.4, 4.7, 4.8$  eV, respectively [24]) as the electrodes. As discussed before,  $C_{48}B_{12}$  and  $C_{48}N_{12}$  have the properties required for proper rectifier behavior. An initial B3LYP/3-21G calculation for the full, connected fullerene/spacer/fullerene system shows that the covalent bond between the spacer and doped fullerenes shifts the electronic structure of the doped fullerenes. However, the HOMO and LUMO of the acceptor-spacer-donor system are still localized on the acceptor and donor sides, respectively, ensuring the desired rectifier behavior. The same properties hold for the acceptor/bridge/donor system [25]. Thus, a smaller threshold voltage for conduction is expected in one direction than in the other direction. As an example, we have investigated the rectifying characteristic of the  $C_{48}B_{12}/C_6H_{14}/C_{48}N_{12}$  system by using non-equilibrium Green function theory in conjunction with a density functional based tight-binding model [26,27]. The rectifier molecule is connected to gold contacts that we treat in the  $s$ -wave approximation with a constant density of states near to the Fermi level [28]. The calculated current/applied potential characteristic is shown in Fig.3(a). A typical rectification characteristic is obtained with a turn-on bias close to the energy difference between  $C_{48}B_{12}$ 's LUMO and  $C_{48}N_{12}$ 's HOMO. Recently, Joachim *et al.* [4] have successfully observed the electrical current flowing through an individual  $C_{60}$  molecule with a scanning tunneling microscope (STM). In light of this progress and the calculated size of  $C_{48}X_{12}$  ( $X=N,B$ ), our rectifier molecule also should be identifiable by STM.

Heterojunctions for molecular electronics can also be formed using  $C_{60-n}X_n$  donors and acceptors. Hybrid nanostructures formed by filling a SWNT with  $C_{60}$  [7] have been observed, and can be superconducting [7] or metallic [29]. Our DFT calculations, done within the local density approximation with double numerical basis including d-polarization function [15,30], show that the incorporation of the  $C_{48}B_{12}$  or  $C_{48}N_{12}$  into a (10,10) [5] or (17,0) [5] SWNT is energetically favorable. About 2.4 eV binding energy per molecule is gained after the  $C_{48}B_{12}$  or  $C_{48}N_{12}$  molecule is inserted periodically inside the SWNTs. In our calculations of doped SWNTs with a one-dimensional periodic boundary condition along the tube axis, three unit cells of a (10,10) tube or two unit cells of a (17,0) tube are included in the supercell with one  $C_{48}B_{12}$  or  $C_{48}N_{12}$ . Charge analysis found that placing an acceptor  $C_{48}B_{12}$  into a (17,0) tube puts a +0.67

$|e|$  charge on the SWNT, while incorporating a donor  $C_{48}N_{12}$  into a (17,0) SWNT puts a  $-0.39 |e|$  charge on the SWNT. Similar results are obtained for a (10,10) SWNT. Hence, putting  $C_{48}B_{12}$  into a semiconducting tube results in a  $p$ -type region on the SWNT, while filling of donors  $C_{48}N_{12}$  into a semiconducting tube leads to a  $n$ -type region on the SWNT. Thus, it is possible to use them to get  $n$ - $p$ - $n$  and  $p$ - $n$ - $p$  transistors [8]. As shown in Fig.3(b), doping a (17,0) semiconducting SWNT with  $C_{48}B_{12}$  and  $C_{48}N_{12}$  should also make a SWNT-based  $p$ - $n$  junction.



**FIG.3:** (a) Calculated current through a rectifier molecule (inset) which consists of  $C_{48}B_{12}$  (left, red for B atoms) and  $C_{48}N_{12}$  (right, blue for N atoms) connected by  $C_6H_{14}$  (middle, green for H atoms) and is coupled to two Au electrodes via S atoms on the two sides. The two C atoms in the ends of the  $C_6H_{14}$  bridge are connected to the N (B) atoms in  $C_{48}N_{12}$  ( $C_{48}B_{12}$ ) respectively. A B3LYP/3-21G calculation shows that the connected rectifier molecular superstructure is stable relative to the separated, individual components by about 19.545 kcal/mol energy. (b) a prototype for  $C_{48}X_{12}@(17,0)$  SWNT-based ( $X=B,N$ )  $p$ - $n$  junction.

In conclusion, we show that acceptor  $C_{60-n}B_n$  and donor  $C_{60-m}N_m$  pairs needed for molecular electronics can be obtained by properly controlling the number  $n$  and  $m$  of the substitutional dopants in  $C_{60}$ . We demonstrated the rectifying characteristic of a molecular rectifier built from our engineered acceptor/donor pairs. Heterojunctions for molecular electronics can be made by inserting these dopants into semiconducting carbon nanotubes. Efficiently synthesizing those acceptor/donor pairs would be of great experimental interest within reach of today's technology. Very recently, small nitrogen-substitutionally-doped fullerenes have been reported, [31] showing experimental progress in this direction.

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