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Selective Interaction of Large or Charge-Transfer Aromatic Molecules with Metallic Single-Wall Carbon Nanotubes: Critical Role of the Molecular Size and Orientation

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Abstract: Using first principles calculations, we report for the first time that large nearly neutral aromatic molecules, such as naphthalene and anthracene, and small charge-transfer aromatic molecules, such as TCNQ and DDQ, interact more strongly with metallic single-wall carbon nanotubes (SWNTs) versus their semiconducting counterparts as the molecular orientation of DDQ is taken into account. Hence two new mechanisms for separating metallic and semiconducting SWNTs via noncovalent $\pi-\pi$ stacking or charge-transfer interaction are suggested.

Single-walled carbon nanotubes (SWNTs) have excellent mechanical and electrical properties that have led to the proposal of many potential applications.[1] However, SWNTs are typically grown as mixtures of metallic and semiconducting tubes, which hurdles their widespread application. Recently, both physical[2,3] and chemical methods[4−8] are developed to separate metallic and semiconductor SWNTs. The chemical method chiefly takes advantage of the difference in adsorption energy of molecules between metallic and semiconducting SWNTs. Theoretically the selective adsorption may occur when the molecules are adsorbed on SWNTs by covalent interaction[8,9] or hydrogen-bond-like linkage.[7,10] It is highly interesting and technically important to explore other forms (especially noncovalent) of selective interaction of substance with SWNTs. SWNTs are considered as an extended π electron system and can combine with other π electron systems, such as aromatic molecules, via $\pi-\pi$ stacking interaction. If the $\pi-\pi$ stacking interaction between SWNTs and aromatic molecules can be described simply by the London formula,[11] aromatic molecules are expected to bind tighter to metallic SWNTs because the polarizability of metallic SWNTs is larger than that of their semiconducting counterparts.[2,6]

In addition, metallic SWNTs have a smaller ionization potential than their semiconducting counterparts, and it is believed that the formation of intermediate charge-transfer complex is responsible for the selective covalent functionalization of diazonium[12] and OsO_2[13] toward metallic SWNTs. When charge-transfer molecules are physisorbed on SWNTs, stronger noncovalent interaction with metallic SWNTs can be anticipated. However, the above expectations are not supported by existing

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theoretical calculations, which demonstrate that neither benzene (C_6H_6)[14,15] nor very strong charge-transfer aromatic molecule 2,3-dichloro-5,-dicyano-1,4-benzoquinone (DDQ:$C_8N_2O_2Cl_2$)[14] selectively interacts with metallic SWNTs. The absence of selective interaction between benzene and SWNTs cannot exclude the possibility of selective interaction of other aromatic molecules with SWNTs. A larger aromatic molecule has a larger polarizability and may be able to detect the difference in adsorption energy between metallic and semiconducting SWNTs according to the London formula. In the previous calculations,[14] the long molecular axis of DDQ is assumed perpendicular to the tube axis for both semiconducting zigzag and metallic armchair SWNTs.[16] When DDQ is placed with the long molecular axis perpendicular to the tube axis of armchair SWNTs, the orientations of the hexagonal carbon rings of DDQ and the SWNT do not coincide, which amounts to ignoring the atomic correlation between the two π electron systems. However, the recent experiments show that the atomic correlation as a commensurate graphene stacking can sometimes overwhelm the elastic force of a graphene layer.[17] Therefore, increasing the size of neutral aromatic molecules and considering the atomic correlation between small charge-transfer aromatic molecules and SWNTs may shed light on the above puzzle.

In this paper, we have studied the interaction of aromatic molecules, benzene (size 4.97×4.30 Å^2), naphthalene ($C_{10}H_8$, size 6.74×4.98 Å^2), 7,7,8,8-tetracyanoquinodimethane (TCNQ: $C_{12}N_4H_4$, size 8.22×4.46 Å^2), and DDQ (size 6.14×5.34 Å^2) with both metallic and semiconducting SWNTs by using the density function theory within the local density approximation. TCNQ is a strong electron acceptor as DDQ. We chose the (10,0) and (6,6) SWNTs with diameters $d = 7.86$ and 8.16 Å, respectively, as representative of semiconducting and metallic SWNTs, respectively. The periodicity of the (10,0) and (6,6) SWNTs is 4.25 and 2.45 Å, respectively. In our supercell model, the periodicities of benzene and DDQ are 3 and 4 times that of the (10,0) and (6,6) SWNT, respectively, while the periodicities of naphthalene and TCNQ are 3 and 5 times that of the (10,0) and (6,6) SWNT, respectively. A large lattice constant is necessary to eliminate the interaction between adjacent aromatic molecules. The separation between aromatic molecules and the wall of the adjacent tube is greater than 6.5 Å. Full geometry optimization was performed for both the atomic positions and lattice lengths by using the ultrasoft pseudopotential[18] plane-wave program, Castep,[19] with two k points. The plane-wave cutoff energy is 240 eV for the complex of SWNT and benzene (naphthalene and TCNQ) and 300 eV for that of SWNT and DDQ, and the static total energies of the relaxed structures are calculated with larger 310 and 380 eV cutoff energies, respectively (for a complex containing O atom, a larger plane-wave cutoff energy is recommended[19]). The convergence tolerance of force on each atom is 0.01 eV/Å. The adsorption energy of aromatic molecules on a SWNT is calculated as $E_{ad} = E(\text{SWNT} + \text{molecule}) - E(\text{SWNT}) - E(\text{molecule})$. Our test calculations on the adsorption of H_2O on the (13,0) and (7,7) SWNTs with a periodicity of 4.25 and 4.50 Å, respectively, show that the changes in E_{ad} are no more than 0.01 eV when the K point number goes from 2 to 5. The double numerical atomic orbital basis set [19] is employed to calculate the electronic energy bands.

The most stable configuration adsorption of benzene on SWNTs is the "bridge" one.[14,15] In accordance with previous calculations,[14,15] benzene shows no selective interaction with metallic SWNTs. The calculated E_{ad} is 0.11 and 0.10 eV for the (10,0) and (6,6) SWNTs, respectively. Two configurations are considered for naphthalene, TCNQ, and DDQ: the long molecular axis is (i) parallel and (ii) perpendicular to the tube axis. Two factors affect the molecular orientation: (1) Effective contact area between the molecule and the sidewall of the tube. When the three molecules are placed with their long molecular axis parallel to the tube axis, the effective contact area is maximized. Therefore, the first factor always drives the long molecular axis parallel to the tube axis. (2) Atomic correlation between the aromatic molecules and the sidewall of the tube. Given the same contact area, the adsorption configuration is most favorable when the orientation of the hexagonal carbon ring of the aromatic molecules is identical with (matches) that on the nanotube sidewall. Therefore, the second factor always drives the hexagonal ring of the aromatic molecules to match that on the nanotube sidewall. When naphthalene and DDQ are placed on the (6,6) SWNT and TCNQ on the (10,0) SWNT in a parallel way, the hexagonal ring of the adsorbed molecules matches that of the sidewall of the SWNTs; thus the parallel orientation should be favored over the perpendicular one in the three cases. In other cases, the favorable orientation depends on the competition of the two factors.

The calculated adsorption energies of naphthalene, TCNQ, and DDQ on the (10,0) and (6,6) SWNTs under different orientations are given in Table 1, with the favorable orientations displayed in Figure 1. As expected, the parallel orientation (the bridge configuration is adopted) is indeed favorable for naphthalene and DDQ on the (6,6) SWNT and TCNQ on the (10,0) SWNT. The difference in E_{ad} between the favorable and unfavorable orientations is small (0.03 eV) for naphthalene on the (6,6) SWNT but up to 0.22 and 0.38 eV for TCNQ and DDQ on the (10,0) and (6,6) SWNTs, respectively. For the adsorption of naphthalene and DDQ on the (10,0) SWNT, the atomic correlation factor is dominant over the effective contact area factor. For the adsorption of TCNQ on the (6,6) SWNT, the two factors balance one another.

One of the most important results from Table 1 is that the adsorption of naphthalene on the (6,6) SWNT (with the lowest E_{ad} of -0.25 eV) is significantly stronger than that on the (10,0) SWNT (with the lowest E_{ad} of -0.15 eV). Inspired by this result, we further investigate the adsorption energy of larger aromatic molecule anthracene ($C_{14}H_{10}$) on SWNTs. In our supercell model, the periodicity of anthracene is 4 and 6 times that of the (10,0) and (6,6) SWNT, respectively. The calculated E_{ad} of anthracene with parallel orientation on the (6,6) SWNT is -0.29 eV, while those with parallel and perpendicular orientations are -0.20 and -0.17 eV, respectively. Hence pure $\pi-\pi$ stacking interaction between nearly neutral (the amount of electron transfer from naphthalene and anthracene to SWNTs is quite small) aromatic molecules and the SWNTs can give rise to a high selectivity of aromatic molecules to the metallic SWNTs

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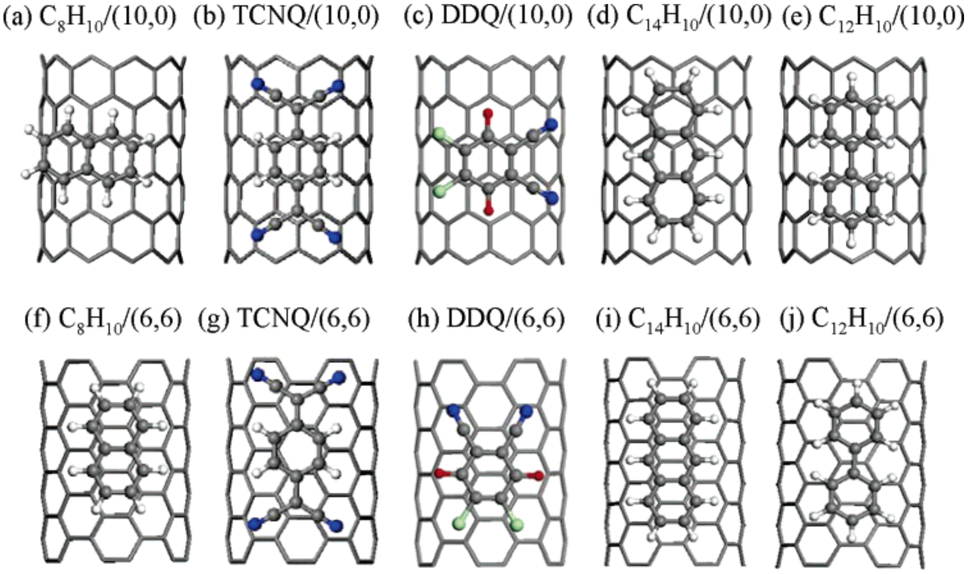
Table 1. Adsorption Energy (E_{ad}), Equilibrium Molecule−Tube Distance (d) (Defined as the Shortest Atom-to-Atom Distance), and Mulliken Charge (Q) of Aromatic Molecules on Outer Surface of the (10,0) and (6,6) SWNTs via Two Orientations: the Molecular Long Axis Parallel and Perpendicular to the Tube Axis; the Calculated E_{ad} of 1,2-Dichlorobenzene on the Pure (8,0) SWNT via $\pi-\pi$ Stacking Interaction Is −0.31 eV[23]

		E_{ad} (eV)		d (Å)		Q (e)	
	Orientation	(10,0)	(6,6)	(10,0)	(6,6)	(10,0)	(6,6)
Benzene		-0.11, -0.20[c]	-0.10,-0.19[c]	3.16	3.28	0.05	0.02
Bibenzene	‖[a]	-0.29 (Mat [d])	-0.27 (Mis)	3.12	3.24	0.03	0.03
	≡[b]	—	-0.14 (Mat)	—	3.08	—	0.05
Naphthalene	‖	-0.14 (Mis [e])	-0.25 (Mat)	3.14	3.14	0.04	0.04
	≡	-0.15 (Mat)	-0.22 (Mis)	3.10	3.16	0.01	0.02
Anthracene	‖	-0.20 (Mis)	-0.29 (Mat)	3.19	3.10	0.03	0.05
	≡	-0.17 (Mat)	—	3.08	—	0.02	—
TCNQ	‖	-0.48 (Mat)	-0.59 (Mis)	3.07	3.18	-0.27	-0.35
	≡	-0.26 (Mis)	-0.59（Mat）	3.09	3.08	-0.10	-0.50
DDQ	‖	-0.57 (Mis)	-1.14 (Mat)	3.10	3.19	-0.32	-0.55
	≡	-0.79, -0.61[f] (Mat)	-0.76 (Mis)	2.89	3.26	-0.27, -0.2[f]	-0.58

[a] The molecular long axis is parallel to the tube axis. [b] The molecular long axis is perpendicular to the tube axis. [c] Reference 15. [d] The hexagonal ring of the aromatic molecule matches that of the sidewall of the nanotube. [e] The hexagonal ring of the aromatic molecule mismatches that of the sidewall of the nanotube. [f] Reference 24.


(a) C_8H_{10}/(10,0) (b) TCNQ/(10,0) (c) DDQ/(10,0) (d) $C_{14}H_{10}$/(10,0) (e) $C_{12}H_{10}$/(10,0)

(f) C_8H_{10}/(6,6) (g) TCNQ/(6,6) (h) DDQ/(6,6) (i) $C_{14}H_{10}$/(6,6) (j) $C_{12}H_{10}$/(6,6)

Figure 1. (Color on line) Optimized favorable adsorption configurations of aromatic molecules on the outside sidewalls of the (10,0) and (6,6) SWNTs. For the adsorption of TCNQ on the (6,6) SWNT, the parallel and perpendicular configurations are degenerate in energy. Grey ball, C; white (small white) ball, H; blue (large black) ball, N; red ball (small black), O; green (large white) ball, Cl.

as the size of the aromatic molecules are large enough (at least containing two hexagonal rings). Interestingly, another larger aromatic molecule bibenzene ($C_{12}H_{10}$) shows no selective interaction with metallic SWNTs (Table 1), and even the adsorption in the (10,0) SWNT is marginally stronger than that on the (6,6) SWNT. The difference in selectivity between naphthalene/anthracene and bibenzene can be ascribed to their different structural character. The effective contact area and atomic correlation are simultaneously optimized on the metallic (6,6) SWNT for naphthalene/anthracene adsorption while these two factors are simultaneously optimized on the semiconducting (10,0) SWNT for bibenzene adsorption. Therefore, the simultaneous optimization of the effective contact area and atomic correlation on metallic SWNTs is the prerequisite of selective adsorption of large aromatic molecules on metallic SWNTs.

An equally important result from Table 1 is that both TCNQ and DDQ also show preferential interaction toward metallic species. For the TCNQ adsorption, the preferential adsorption toward metallic SWNTs occurs regardless of the molecular orientation. In the DDQ case, the preferential adsorption only occurs as the molecular orientational effect is taken into consideration; the perpendicular displacement of DDQ on the (10,0) and (6,6) SWNTs gives rise to a similar adsorption energy ($E_{ad} = -0.79$ and -0.76 eV for the (10,0) and (6,6) SWNTs, respectively), as reported in previous calculations.[14] The favorable adsorptions of TCNQ and DDQ on the (6,6) SWNT are 0.11 and 0.38 eV stronger than those on the (10,0) SWNT, respectively. The remarkably higher selectivity of DDQ to metallic SWNTs than TCNQ is ascribed to the fact both the effective contact area and atomic correlation can be optimized when DDQ is adsorbed on the (6,6) SWNT. The interaction between charge-transfer aromatic molecules and SWNTs is considered as a mixture of $\pi-\pi$ stacking interaction and charge-transfer (electrostatic) interaction. It appears that mere $\pi-\pi$ stacking interaction between TCNQ(DDQ) and SWNTs could not lead to selective interaction, since both TCNQ and DDQ

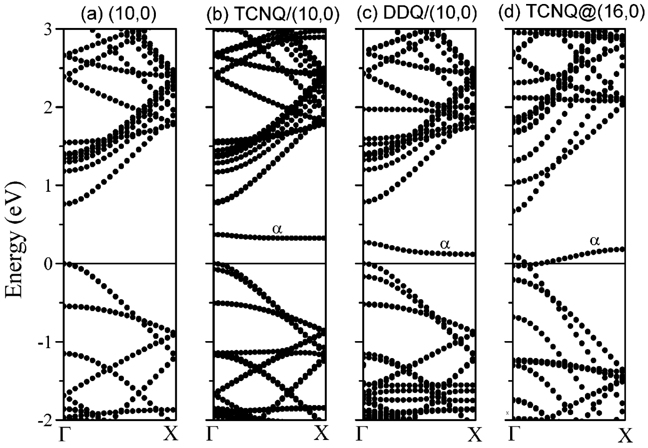


Figure 2. Electronic structures of the (a) pure (10,0) SWNT, (b) TCNQ exohedrally doped (10,0) SWNT, (c) DDQ exohedrally doped (10,0) SWNT, and (d) TCNQ endohedrally doped (16,0) SWNT. The LUMO-derived orbitals for the aromatic molecules are labeled by α. The Fermi level is set to zero.

only contain one hexagonal carbon ring as benzene does. The calculated charges of aromatic molecules adsorbed on SWNTs from Mulliken population analysis are also provided in Table 1. The amount of charge transfer from the (6,6) SWNT to the most stable TCNQ and DDQ is 0.35−0.50 and 0.55 *e* respectively, whereas the amount from (10,0) SWNT to them is only 0.27 *e*, nearly half of the former case. The selective interaction of charge-transfer aromatic molecules with metallic SWNTs is thus attributed to the larger amount of charge transfer from metallic SWNTs to charge-transfer aromatic molecules. The support to the stronger interaction of charge-transfer aromatic molecules toward metallic SWNTs versus their semiconducting counterparts is found in a very recent experiment,[20] which observed preferential reactivity of charge-transfer organic molecules (including TCNQ) toward smaller band gap SWNTs versus larger band gap SWNTs.

The electronic band structures of TCNQ and DDQ exohedrally doped (10,0) SWNTs (represented by molecule/(10,0)) are displayed in Figure 2b and c, respectively. The two complexes remain semiconductors with reduced energy gaps due to the appearance of novel bands, derived from the lowest unoccupied molecular orbital (LUMO) of TCNQ and DDQ, in the band gap of the (10,0) SWNT. The $\pi-\pi$ stacking interaction lifts the degeneracy of the (10,0) nanotube on the valence band top. Recent experiment[21] and theoretical calculations [22] revealed that doping of TCNQ on the inside of semiconducting SWNTs has led to *p*-type doping of semiconducting SWNTs. In that theoretical work,[22] the periodicity of the TCNQ molecule is assumed to be twice that of the (16,0) SWNT (thus the center-to-center distance between TCNQ molecules is 8.50 Å) and each supercell contains 148 atoms. Each TCNQ molecule is assumed to make an angle of about 30° with the tube axis to maintain a proper spacing between molecules. The most favorable position of the TCNQ molecule inside the (16,0) SWNT is the tube center. The electronic band structure of TCNQ endohedrally doped (16,0) SWNTs (represented by TCNQ@(16,0)) is provided in Figure 2d, which is distinct from that of TCNQ/(10,0). The endohedral TCNQ LUMO-derived band does overlap with the valence band of the tube near the Γ point, and about 0.32 electrons on the valence band on top of the tube are transferred to the TCNQ LUMO-derived band. This difference in electronic structure between TCNQ exohedrally and endohedrally doped semiconducting SWNTs is ascribed to the fact that the strong $\pi-\pi$ stacking interaction between SWNT and outside TCNQ gives rise to much stronger orbital hybridization between SWNT and TCNQ (correspondingly a much stronger energy band repulsion between the TCNQ LUMO-derived band and the tube valence band) than the interaction between SWNT and inside TCNQ (it is not $\pi-\pi$ stacking type). Figure 3a−c show the isosurfaces of the squared wave functions of the LUMO-derived bands of aromatic molecules at the Γ point for TCNQ/(10,0), DDQ/(10,0), and TCNQ@(16,0), respectively. Many more tube orbital components are mixed into the TCNQ and DDQ LUMO-derived bands in the exohedral doping case than in the endohedral doping case. The hybridization between acceptor aromatic molecules and SWNTs is stronger when acceptor aromatic molecules are adsorbed on the outside sidewall of metallic SWNTs. Even the dispersion of one conduction band of the (6,6) SWNT has been altered completely, as shown in Figure 4.

The most important potential application of selective interaction of larger nearly neutral or charge-transfer aromatic molecules toward metallic SWNTs is the separation of metallic and semiconducting SWNTs. The calculated E_{ad} of NH_2CH_3 on the semiconducting (13,0) SWNT is 61% of that on the metallic (7,7) SWNT, and this high selectivity leads to enrichment of metallic SWNTs with concentrations up to 87% in amine-assisted separation.[7] The calculated E_{ad} of naphthalene, anthracene, TCNQ, and DDQ on the semiconducting (10,0) SWNT is 60%, 69%, 81%, and 69%, respectively of that on the metallic (6,6) SWNT; thus comparably high separation efficiency is anticipated in naphthalene, anthracene, and DDQ-assisted separation.

In summary, the $\pi-\pi$ stacking interaction between nearly neutral aromatic molecules and SWNTs becomes dependent on the electronic structure of SWNTs as the molecular size is large enough and the effective contact area and the atomic correlation are simultaneously optimized on metallic SWNTs from our first principles calculations. The interaction between small charge-

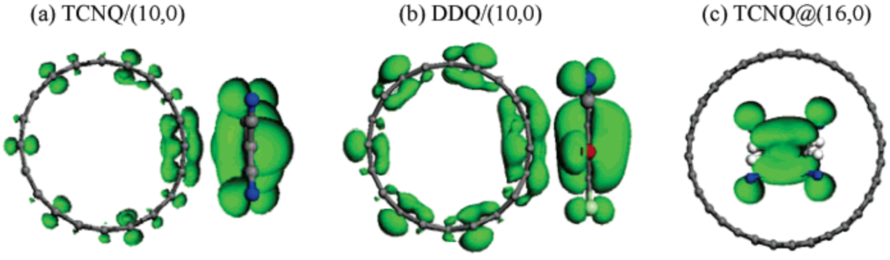


Figure 3. (Color on line) Isosurfaces of the squared wave functions of the LUMO-derived bands at the Γ point for the aromatic molecules adsorbed on the (a and b) outside and (c) inside surfaces of the SWNTs. The isovalue is 0.012 au.

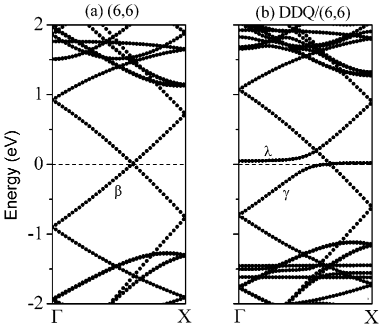


Figure 4. Electronic structures of the (a) pure and (b) DDQ exohedrally doped (6,6) SWNTs. The two emerging bands from a strong hybridization between one conduction band of the nanotube (labeled by β) and the DDQ LUMO-derived band are labeled by γ and λ, respectively. The Fermi level is set to zero.

transfer aromatic molecules and SWNTs is dependent on the electronic structure of SWNTs too and sensitive to the molecular orientation. The remarkably high selectivity of naphthalene, anthracene, and DDQ molecules toward metallic SWNTs suggests two novel routes for separating metallic from semiconducting SWNTs via $\pi-\pi$ stacking interaction or charge-transfer interaction. Since the two kinds of selective interactions are noncovalent, the adsorbed aromatic molecules can be easily removed after completion of a separation procedure.

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Supporting Information Available: Complete ref 7 and an explanation of why a large aromatic molecule can more easily detect the difference in adsorption energy between metallic and semiconducting SWNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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