

Models for the Structure and Electronic Transmission of Carbon Nanotubes Covalently Linked by a Molecular Bridge via Amide Couplings

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Strong covalent bonding between molecules and conductors offers the promise of enhanced contacts compared to those produced by physisorptive or weak thiol-like chemisorptive processes; such connections have recently been realized through the covalent bridging of carboxylic-acid terminated carbon nanotubes (Guo, X.; Small, J. P.; Klare, J. E.; Wang, Y.; Purewal, M. S.; Tam, I. W.; Hong, B. H.; Caldwell, R.; Huang, L.; O'Brien, S.; Yan, J.; Breslow, R.; Wind, S. J.; Hone, J.; Kim, P.; Nuckolls, C. *Science* **2006**, *311*, 356). We simulate possible chemical structures and charge-transport properties of these structures, using a simple benzene linker attached through amide bonds to reconnect the cut nanotube halves. The results show that rigid, high-transmission junctions are feasible but a multitude of binding chemistries and geometries are possible. Chemical changes in the vicinity of the junction are shown to control the tunneling barrier, suggesting applications of these devices as chemical sensors and electronic logic units.

Achieving good electric contacts between a molecule and electrodes is a challenge in molecular electronics. Recently it has been demonstrated that this can be achieved by covalently bonding a molecule between carbon nanotubes¹ using stable and well-controlled amide-group linkers. This may prove to be an alternate approach to the commonly used gold–thiol linker junction, a junction whose properties are poorly controlled as (i) the linkage is of only moderate strength and can adopt a multitude of different structural conformations, and (ii) the gold surface can readily reconfigure and reshape under the influence of chemisorption and applied electric fields.^{2,3} Good connects require both low electrical resistance and high structural resilience, and their establishment is an important step for realizing circuitry built from single molecules. In this work, we describe the properties of some simple model systems designed to identify key structural aspects for the nanotube amide junctions that have been synthesized,¹ junctions for which detailed atomic-level structural information is not yet available experimentally. One such structural model is shown as an example in Figure 1. We simulate using first-principles electron-transport techniques the electrical characteristic of such molecular junctions, investigating how chemical variations in the junction control the number of available conduction channels and the height of the tunneling barrier.

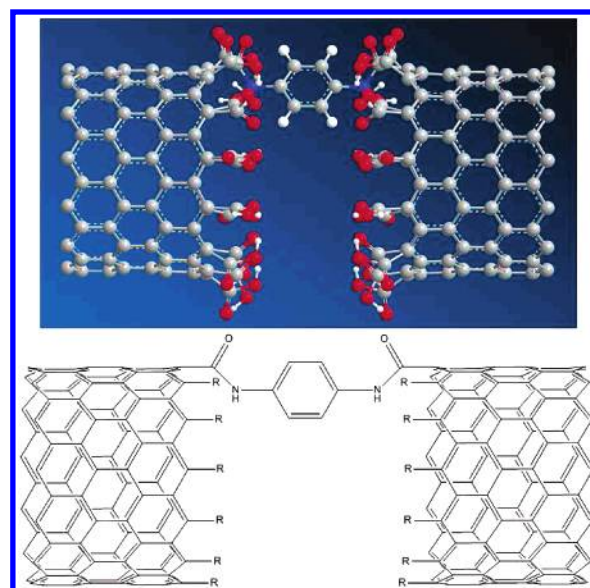


Figure 1. PM3-optimized structure of the system SWNT(13,0)–(COOH)₁₂–CONH–C₆H₄–NHCO–(COOH)₁₂–SWNT(13,0) embodying one diaminobenzene linkage connecting the two COOH-terminated halves of a cut (13,0) SWNT.

Covalently bridged nanotubes have been prepared¹ by taking a single-walled carbon nanotube (SWNT), cutting the tube in two with a beam of oxygen atoms under ultrahigh vacuum, and then exposing the tubes to a solution containing long molecules with amine groups attached to each end, thus rejoining the two halves of the original SWNT. It is thought that under these conditions the cut SWNT ends become terminated with carboxylic acid groups, and that the reconnection involves amide-formation reactions involving water elimination.^{1,3–5}

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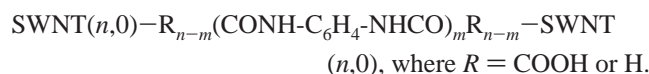
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The junction shown in Figure 1 is one of the simplest structures possible that embodies these features. Straight cuts are made to the original SWNT, the ensuing reactive nanotube ends are fully terminated with COOH groups, only one amide-linked bridge molecule is added, and this bridge molecule consists of just a single benzene ring. While much longer bridging molecules have been used in experiments, this model system should embody most of the interesting molecular properties while providing a much simpler system to compute and understand. One can envisage the atom beam making instead jagged cuts to the SWNT, and many different reactions are possible to stabilize the cut ends of the tube. An undesired property of the structure shown in Figure 1 is that its many COOH groups are in close proximity to each other but cannot form intramolecular hydrogen-bonds due to the large steric forces that oppose the required conformational changes. No doubt solvation effects are very important in determining the chemical nature of the cut ends, but these are very complex and are not feasible to include in a realistic way at the present time. To obtain a qualitative indication as to the likely magnitude of termination effects on the cut SWNT ends, we consider a second model system in which only one COOH group forms per cut SWNT end with simple hydrogen termination occurring at all other cut sites. Also, while the cut SWNTs can be of all types and sizes, we consider only tubes of the $(n,0)$ form, considering explicitly the semiconducting (13,0) and conducting (12,0) nanotubes. These tubes have sizes comparable to those used in the experiments,¹ ca. a diameter of 1.02 nm for the (13,0) SWNT. Finally, we investigate the effect of multiple molecules bridging the cut by taking the fully COOH-terminated (12,0) SWNT and bridging it with $m = 0, 1, 2, 3, 4, 6,$ or 12 amide-coupled benzene molecules in parallel. All systems studied have the general structure:



Optimized geometries for the bridged $(n,0)$ SWNTs considered were obtained using the parametrized model number 3 (PM3) method⁶ with the Gaussian-03 program package.⁷ During this geometry optimization process, $4n$ carbon atoms were included explicitly representing the SWNTs at each end of the molecule with these corresponding to only the terminal two rings apparent in Figure 1. These SWNT atoms were hydrogen terminated at one end to mimic the remainder of the semi-infinite nanotube, and the coordinates of these terminating atoms plus the nearest $2n$ carbon atoms were frozen during the optimization. The cut ends of the nanotubes were bridged with the CONH-C₆H₄-NHCO linkages and the remaining SWNT sites terminated with either COOH or H groups. During the optimization, all coordinates of the amide linkages, the COOH or H terminating groups on the cut ends, and the nearest $2n$ carbon atoms per SWNT were allowed to relax. A variety of initial structures were prepared for optimization, these differing in the orientations of the COOH groups and the amide linkages. It is clear that a significant number of low-energy conformations exist for the structure depicted in Figure 1, as indeed they do for all molecules with COOH termination. While proper treatment of this feature requires full sampling of the available configurations at the reaction temperature, in this work only the lowest-energy configuration obtained is selected and investigated for its conductivity properties.

The transmission of electrical current through the bridged junctions was evaluated using our package MATDICAL⁸ at very low bias voltage. In this fully self-consistent nonequilibrium

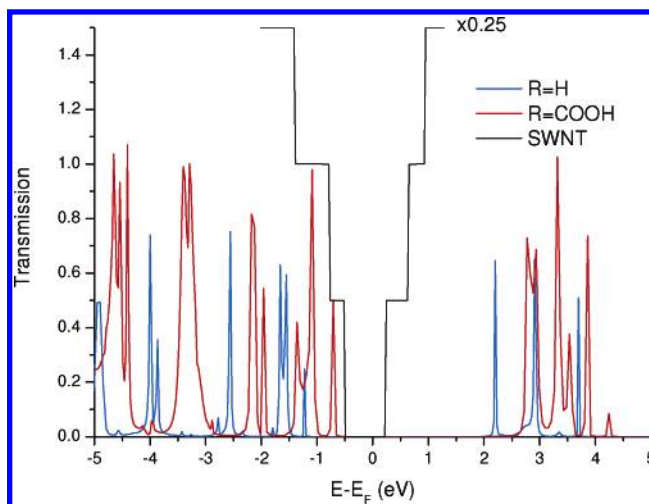


Figure 2. The transmission probability for an electron at energy E through an infinite semiconducting (13,0) SWNT (black) compared to that through a cut (13,0) SWNT that has been rejoined using a single amide-coupled benzene unit, SWNT(13,0)-R₁₂-CONH-C₆H₄-NHCO-R₁₂-SWNT(13,0), with $R = \text{COOH}$ (red) or $R = \text{H}$ (blue).

Green's function^{9,10} (NEGF) density functional theory (DFT) first-principles method, all the atomic-level details of the system were considered. We used standard norm-conserving pseudo-potential¹¹ and s, p, d single- ζ basis set within the local-density approximation. However, the density functional used in the calculations was obtained using the computationally efficient Goedecker approximation¹² to fit the standard PW91 generalized-gradient-approximation density functional.¹³ Atomic coordinates for these calculations were obtained by taking the Gaussian-optimized coordinates for the truncated SWNT-molecule-truncated SWNT device. For the transport analysis, we take the optimized SWNT-molecule-SWNT structure discussed above, removing the terminating hydrogen atoms at the outer end of the two SWNTs, and then extending the SWNTs to left and right infinities so that the two SWNTs become the leads of the molecular device. The semi-infinite nature of the electrodes was then included using self-energy corrections applied to these $4n$ atoms; details of the methods used to implement this have been described previously.⁸

Shown in Figure 2 is the calculated transmission through the system SWNT(13,0)-(COOH)₁₂CONH-C₆H₄-NHCO(COOH)₁₂-SWNT(13,0) depicted in Figure 1 made using a cut (13,0) semiconducting nanotube, a single bridging molecule, and full COOH termination of the cut nanotube ends. The transmission is shown as a function of the difference $E - E_F$ between the energy E of the conducting electron and the Fermi energy E_F of the system. The resonant tunneling process is responsible for the sharp peaks in the transmission coefficient as a function of electron energy. The quantized conductance for an infinite (13,0) carbon nanotube also is shown in Figure 2; the finite band gap of the semiconductor is apparent, but it is clear that the nature of the transmission is controlled not by the properties of the SWNT but rather by the properties of the molecular bridging region. Note that similar calculations performed on a purely COOH terminated cut SWNT without the presence of the amino-coupled bridging molecule ($m = 0$) result in negligible predicted transmittance. Also shown in the Figure is the transmission calculated for the system in which the terminating COOH groups not associated with amide formation are replaced with H atoms. Changing this chemical property is seen to have a profound effect on the calculated transmission through shifts in the resonance energies, changes to the resonance widths, and changes to the resonance patterns that

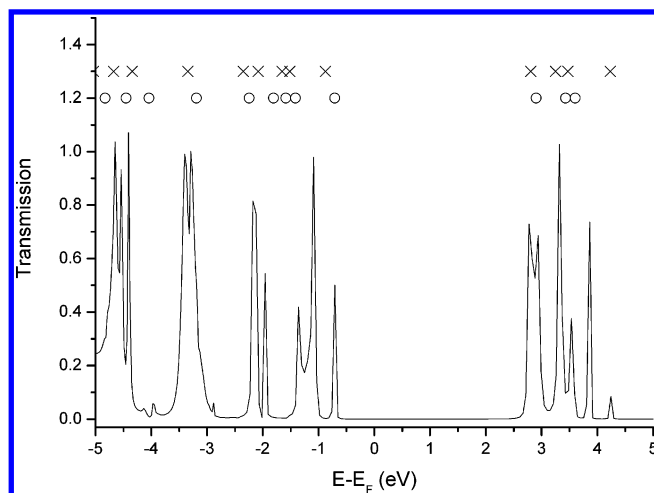


Figure 3. The peaks in the transmission probability for an electron at energy E through SWNT(13,0)-(COOH)₁₂-CONH-C₆H₄-NHCO-(COOH)₁₂-SWNT(13,0) are compared to the aligned molecular-orbital eigenvalues for HCONH-C₆H₄-NHCOH obtained without (x) and with (o) consideration of the effects of the electric field emanating from the SWNT(13,0)-(COOH)₁₂ units.

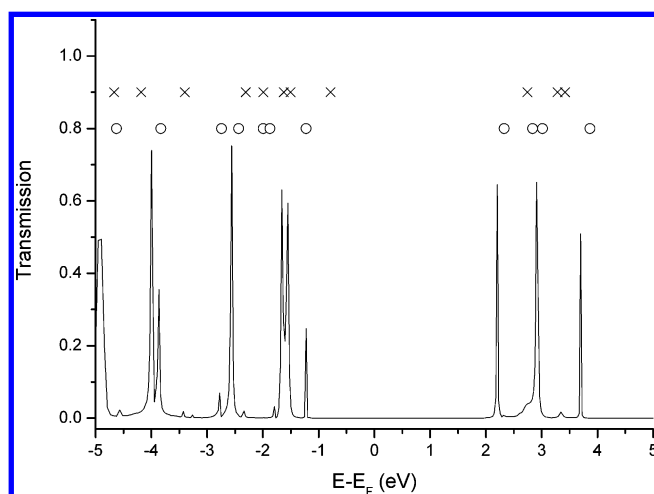


Figure 4. The peaks in the transmission probability for an electron at energy E through SWNT(13,0)-H₁₂-CONH-C₆H₄-NHCO-H₁₂-SWNT(13,0) are compared to the aligned molecular orbital eigenvalues for HCONH-C₆H₄-NHCOH obtained without (x) and with (o) consideration of the effects of the electric field emanating from the SWNT(13,0)-H₁₂ units.

are particularly noticeable at high energies. Because of the broader resonance widths and closeness of the first resonance peak to the SWNT band edge, the COOH terminated SWNT is expected to provide enhanced low-voltage operational characteristics for the device.

The effects of SWNT termination on the conduction characteristics can be understood in terms of the influence of the electric field emanating from the terminating groups on the properties of the bridging molecule. In Figures 3 and 4, the transmission characteristics of the two bridged (13,0) SWNTs from Figure 2 are reproduced at higher energy resolution and compared to the in situ calculated molecular orbital energies of the bridging molecule. These energies are obtained by taking the full molecular system and replacing the SWNT atoms to which the amide linkages attach with hydrogen atoms. This forms a new molecule of the form HCONH-C₆H₄-NHCOH for which the molecular orbital energies are determined by Gaussian-03⁷ using the PW91 density functional¹³ with the

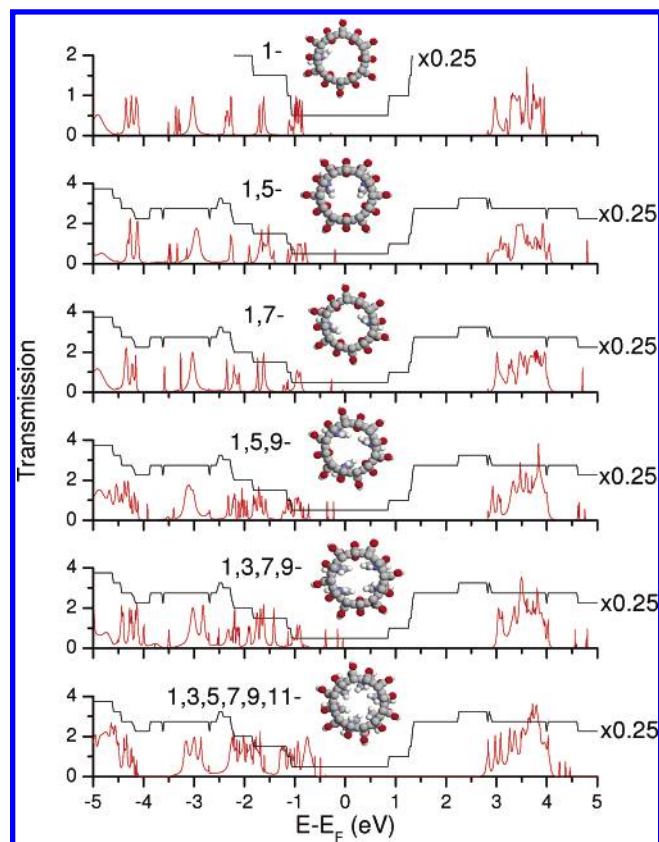


Figure 5. The transmission probability for an electron at energy E through an infinite metallic (12,0) SWNT (black) compared to that through a cut (13,0) SWNT rejoined by $m = 1-6$ amide-coupled benzene units, SWNT($n,0$)-(COOH) _{$n-m$} -(CONH-C₆H₄-NHCO) _{m} -(COOH) _{$n-m$} -SWNT($n,0$) (red); the inserts show the optimized structures looking down the axis of the nanotube.

6-31G* basis set.¹⁴ Evaluated at this level, the calculated molecular energy levels are affected only by the molecular geometry, a feature that differs slightly for the two systems considered. The deduced molecule-only energy levels shown in Figures 3 and 4 are very similar, indicating that geometrical distortions have only a minor influence. The effect of the electric field emanating from the SWNT and its COOH or H terminal groups on the energy levels of the bridging molecule is then made manifest through re-evaluation of the orbital energies for the HCONH-C₆H₄-NHCOH molecule in the presence of external charges placed on every nonbridge atom of the full SWNT(13,0)-R₁₂-(CONH-C₆H₄-NHCO) _{m} -R₁₂-SWNT(13,0) system. These point charges were determined from a Mulliken analysis of the PM3 electron density of the full system. Also shown in Figures 3 and 4 are the energy levels in the presence of this external field, and these are seen in the Figures to depend strongly on the nature of the SWNT termination and to correlate with the calculated shifts in the peaks of the calculated transmission functions.

The transmissions calculated through a (12,0) conducting SWNT that has been split and rejoined by $m = 1$ to 6 diaminobenzene linkers are shown in Figure 5. The most significant qualitative difference of these results from that shown previously for the semiconducting nanotube in Figure 2 is the lack of a band gap in the transmission of the nanotube and the appearance of low-energy through-bridge conduction pathways that access this SWNT conductivity. As a result, the conductivity of bridged conducting nanotubes is expected to significantly exceed that of bridged semiconducting ones.

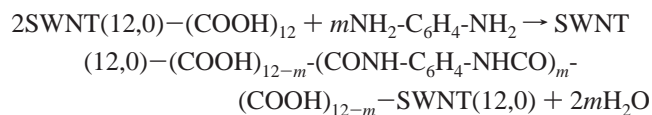
TABLE 1: The Energy of Reaction $\Delta\Delta U$ in kcal mol⁻¹ for the Sequential Addition of Diaminobenzene Linkers to Rejoin a Cut (12,0) SWNT, as Evaluated Using PM3 for Gas-Phase Samples

m_1	m_2	arrangement	$\Delta\Delta U$
0	1	1-	2
1	2	1,2-	21
1	2	1,3-	2
1	2	1,5-	1
1	2	1,7-	0
2	3	1,3,5-	9
2	3	1,5,9-	4
3	4	1,3,5,7-	13
3	4	1,3,7,9-	9
4	6	1,3,5,7,9,11-	18
6	12		72

So far we have considered the possibility that only one diaminobenzene molecule bridges the split SWNT. While multiple bridges could be established in a very large number of ways, we consider only regular arrangements in which the bridging molecules assemble parallel to each other. Even with this restriction, multitudes of possibilities still arise, however, and we proceed by optimizing as before the energies of a range of conformations for each isomer considered and report results for only the lowest-energy structures found.

Two low-energy arrangements corresponding to the 1,5- and 1,7- dibridged species ($m = 2$) are shown in Figure 5, along with their calculated electronic transmissions. Most significantly, the transmissions rise toward values of 2, indicating that both bridges act independently to facilitate conduction through the junction. Further, the lowest-energy conduction channel appears significantly closer to the Fermi energy than it does for the monobridged SWNT, indicating additional enhancement of the low-voltage conductivity. Shown also in the Figure 5 are results for the lowest energy tri-, tetra-, and hexabridged structures found. As the number of bridging units increases, the number of available channels continues to increase in certain energy regions but in general these further enhancements are small, indicating that interference between the channels does become significant. However, the density of low-energy channels continues to increase with increased bridging. We find a distinct difference between single-bridged and multiple-bridged structures, with transmission peak values $1G_0$ and $2G_0$. This may provide a criterion for estimate in the experimental situation. In addition, we do not observe a proportionality for the electron tunneling transmission and bridging molecule number.

While steric constraints are often used experimentally to minimize the possibility of multiple bridging,¹ multiple bridging is also a studied phenomenon.¹ Their likelihood can be best estimated computationally through consideration of the energies required for the successive addition of amide linkages. If the energies for multiple bridge formation for the complex reaction



are ΔU_m , then the energies for successive bridging going from bridging of extent m_1 to bridging of extent m_2 are given by

$$\Delta\Delta U = (\Delta U_{m_2} - \Delta U_{m_1}) / (m_2 - m_1)$$

The results obtained for a variety of bridge arrangements, including those depicted in Figure 5, are given in Table 1. They predict that addition of the first bridging molecule is slightly

endothermic, but this is not expected to be a reliable estimate of the thermodynamics owing to the limitations of the PM3 method and the neglect of solvent interactions. More significantly, the calculations predict that addition of a second bridging unit requires only the same amount of energy as the first, provided that the bridges are well separated, as in the case of the 1,7-arrangement. Subsequent additions of the bridging molecule are predicted to be less likely, however, presumably because of the increase in repulsive interactions between the bridges. There appears to be a significant energy penalty associated with the assembly of two bridging molecules on adjacent SWNT sites, as indicated in Table 1 by the large positive values of $\Delta\Delta U$ for the 1,2-dibridged species and for the dodecyl-bridged species.

In summary, the results obtained indicate that molecular devices involving amide-linked molecules spanning gaps between SWNTs offer good current transmission properties and may be useful in solving the problem of establishing good electrical contact between conductors molecules. These systems also offer advantages over more commonly used scenarios such as gold–thiol–molecule–thiol–gold structures¹⁵ in that strong covalent bonds form that do not dynamically reconfigure, giving rise to junctions that are structurally stable. However, we find that the amide linkages still continue to support a large range of attachment chemistries and geometries, a property that is most likely to lead to poorly reproducible characteristics within an ensemble of junctions. Further, unless steric control measures are implemented¹ the production technique of cutting SWNTs with an O atom beam followed by amide-formation reactions will not necessarily lead to reproducibility in the number of bridges that form across the cut. We have shown that the chemical and structural nature of the attachment, as well as the number of bridges that form, are significant quantities as they modulate the device transmission characteristics. If the means can be obtained for reproducibly creating the interface chemistry and structure, then these properties would become very useful in the development of device applications. Chemical reactions at or near the interface will significantly influence the conductivity through the demonstrated effect of environment on the tunneling barrier height, allowing for the direct possibility of building single molecule detectors. This effect can operate either as an alternative to or cooperatively with chemical control of conductivity through reactions directly on the bridging molecule.¹ Similarly, the demonstrated sensitivity of the transmission to electric fields opens up the possibility of controlled switching of molecular-electronic circuitry.

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