Tailoring electronic and charge transport properties of molecular π-stacked heterojunctions

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(Received 25 November 2005; accepted 13 June 2006; published online 31 August 2006)

The electronic structure and charge transport properties of π-stacked heterojunctions formed by two different 3,6-R2–1-ethynaphthalene (R: H, CH3, Cl) fragments have been investigated with a tight binding method. The extent of the evanescent wave function that escapes across the interface near $E_F$ is shorter when chloride groups are used to modify the π-electron distribution of the naphthalene core than when methyl groups are used. Consequently, the tunneling of carriers in CH3-heterojunction is significantly larger than for systems containing chloride groups. This shows that specific electronic properties can be tailored on naphthalene-based assemblies in which a judicious combination of functional groups is considered. © 2006 American Institute of Physics. [DOI: 10.1063/1.2266228]

The control of supramolecular architecture constitutes a major challenge in the development of high performance organic semiconductor devices.1 Organic semiconductors that exploit the stacking of conjugated polymers and molecules in which significant intermolecular π-electron coupling exists constitute a promising class of materials.2,3 Different approaches for creating low-dimensional assemblies with tailored structural properties favoring π stacking are emerging.4,5 One promising approach is self-directed assembly on a hydrogen-passivated Si(100) surface where molecular lines or wires of styrene have been created through a chain reaction growth mechanism.5,6 The main interest for Si surface is clear that it is widely used in the fabrication of electronic devices, but an additional advantage of Si(100) is the distance separating surface Si atoms (3.8 Å) which favors π-electron coupling between molecules covalently attached on the surface.7 As the chain reaction can, in principle, be controlled through the concentration of reactants, this approach appears well adapted to the creation of molecular heterojunctions made of similar molecules with different functional groups. This opens an opportunity to build electroactive organic materials (transistor and diode) at a molecular resolution, and more importantly to design their electronic and electrical properties.

Here we present the results of tight binding calculations of the electronic structure and charge transport characteristics of molecular model systems (see Scheme 1). Our aim is to compare homo- and heterowires containing simple functional groups, such as CH3, Cl, and H, and to identify the more promising avenues to produce electroactive molecular systems where π-electron charge density can precisely be tuned by a judicious choice of the substituents on a π-rich molecule. The model is based on the lateral stacking of 1-ethyl-naphthalene (eNap) and 3,6-R2–1-ethynaphthalene (R2-eNap) molecules into an ordered one-dimensional (1D) assembly. Naphthalene is representative of a general class of π-delocalized systems, and the functional groups R are chosen for their donor-acceptor properties to influence the π-electron density of naphthalene. The separation between molecules within the assembly was fixed at 3.8 Å. This distance mimics the separation between Si dimers on the Si(100)[2 × 1] surface.

The electrical transport properties of 1D structures were computed using Green’s function approach within the Landauer-Büttiker formalism.5,9 Following this formalism, we express the transmittance $T(E)$ as the summation of transmission probabilities over the conduction channels between the metallic contacts.10 A transmission probability of one is associated with a ballistic charge transport. The charge transport properties were evaluated in the stacking direction by placing a gold electrode composed of a plane of 29 Au atoms with (111) crystal arrangement at both ends of the stack [d(Au-eNap)=2.0 Å]. The metallic contacts consist of a sufficient number of Au atoms to create a large contact area relative to the junction ends, and the short d(Au-eNap) distance was chosen to minimize contact resistance.5,9 In contrast to bulk materials11 and to single molecule devices,12 the influence of the gold electrodes on the electronic structure of such π-stacked arrangement occurs within the very first connected molecules. For systems containing ten or more molecules, we can confidently place the Fermi energy at the midgap of the assembly. The electronic structure and charge transport calculations were performed with a tight binding method13 [extended Hückel theory EHT] that can reproduce, at least qualitatively for similar molecular species, the results of more accurate computational techniques, such as density functional theory.14

Figure 1 gives the variation of the band gap for homowires and heterojunctions as a function of the size of the 1D assemblies. The lower panel considers methyl (CH3) as a

SCHEME 1. Representation of a small arrangement of 3,6-R2–1-ethynaphthalene molecules in the heterojunction structure, where $R$=CH3 or Cl, or H in e-Nap. Molecules in this perfectly stacked assembly are separated by 3.8 Å, which is the Si–Si distance in the dimer row direction of the Si(001) [2 × 1] surface.

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substituent, while chloride (Cl) group has been investigated in the upper panel. In general, the variation of the band gap value initially shows a sharp decrease but then slowly converges to a stable value with increasing molecular wire length. This decrease is clearly related to an increasing inter-action between π electrons of the molecules. In addition, the band gap obtained for a molecular assembly containing at least ten molecules reproduced the values calculated for periodic 1D molecular systems. Although the presence of methyl groups in (CH$_2$)$_n$-eNap provokes a significant charge redistribution within the naphthalene backbone, the band gap and the position of frontier orbitals [highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)] remain almost unchanged. The presence of methyl groups on naphthalene closes the gap by less than 1% on a 20 molecule system (see lower panel) compared to the eNap homowire. In addition, the band gap variation for the heterojunction containing both eNap and (CH$_2$)$_n$-eNap molecules is very similar to the one just described for the eNap and (CH$_2$)$_n$-eNap homowires. In contrast, for the eNap/Cl$_2$-eNap heterojunction, the influence of chlorine on the electronic property of the eNap fragment is much more pronounced than that of methyl. When going from the eNap to the Cl$_2$-eNap assembly, the band gap decreases by more than 10% for systems with more than 20 molecules. The smaller band gap found for the eNap/Cl$_2$-eNap heterojunction, and to a lower extent for the eNap/CH$_3$-eNap, is related to the partial localization of HOMO (LUMO) on the R$_2$-eNap (eNap) fragment in the assembly, as discussed below.

Figure 2 compares the wave function contours of HOMO and LUMO for (a) eNap, (b) eNap/(CH$_2$)$_2$-eNap, and (c) eNap/Cl$_2$-eNap. We can appreciate the importance of π-electron coupling between molecules through the delocalization over the entire eNap homowire (a) and over individual segments in the heterojunctions [b] and (c)]. We need to emphasize that HOMOs (LUMOs) are π-resonant states at the top (bottom) of the valence (conduction) band of the π-stacked systems. We previously demonstrated that π-electron delocalization, as well as electron transport, through a perfect 1D assembly such as in Fig. 2(a) mostly depends upon the coupling between π orbitals of individual molecules, to finally create π-resonant states. The localization of the wave function on specific fragments also suggests that the heterojunction could act as an intrinsic diode in which the carrier propagates in a single direction, drastically unlike the homowire in which the wave function is totally delocalized.

The existence of an evanescent wave function near the Fermi energy, which crosses the interface and significantly penetrates into the opposite segment, can easily be observed in Fig. 2. It is clear that such an evanescent wave function would constitute a preferential and efficient channel for electron or hole propagation by tunneling. For eNap/(CH$_2$)$_n$-eNap [see Fig. 2(b)], the wave function extends over almost the entire opposite segment. As in the eNap/(CH$_2$)$_n$-eNap system, the HOMO and LUMO of eNap/Cl$_2$-eNap are strongly localized on the Cl$_2$-eNap and eNap fragments, respectively. The extent of localization is more important for Cl$_2$-eNap than for (CH$_2$)$_n$-eNap. This is particularly clear for the LUMO where the wave function emerging from the eNap segment rapidly drops within the very first molecular units of the Cl$_2$-eNap segment [see Fig. 2(c)]. In short, HOMO and LUMO wave functions are more strongly localized in R=Cl than in R=CH$_3$ heterojunction, and this has an important impact on the associated transport properties.

Figure 3 compares the density of states (DOS) of eNap, R$_2$-eNap, and eNap/R$_2$-eNap assemblies containing ten molecular units along with their corresponding transmittance T(E). The nature of the frontier orbitals localized on either side of the heterojunction can be identified in the DOS diagrams: the HOMO is centered on eNap while the LUMO is associated with the R$_2$-eNap moiety. The DOS for the heterojunction basically shows a simple superposition of individual contributions of eNap and R$_2$-eNap without significant peak displacement. Due to the absence of shifts in peak positions and intensities, we do not anticipate a significant charge transfer between the different fragments of the molecular junction. Thus, the simple population analysis of the charge distribution determined from EHT and more accurate Hartree-Fock (HF/6-31G) calculations does not indicate any charge transfer between molecules within homowires nor between segments in the heterowires. Although the variation of the band gap with the size of the assembly clearly reveals the existence of intermolecular interactions, these are not related...
to a charge transfer mechanism but to an improved π-electron coupling in such highly packed assemblies.

Several observations can be drawn from the transmittance curves shown in Fig. 3. First, there is very low $T(E)$ near $E_F$ and very sharp modulation of the $T(E)$ over several peaks at higher energy. The low $T(E)$ at $E_F$ reveals that the molecules are not chemically bonded, and indicates that in the absence of conducting channels, these systems may be compared to a series of individual conductors separated by 3.8 Å. In contrast, the sharp transmittance modulations observed at HOMO and LUMO energies, are essentially related to the existence of π-resonant states over the assembly and between molecules which allows transport of carriers by resonant tunneling. The electron transport in absence of π-electron coupling between molecules in this assembly would be compatible with a charge hopping transport in which $T(E)$ would be very low, and where band dispersion in the propagation direction is practically absent.

The variation in $T(E)$ as a function of energy from eNap to eNap(CH$_3$)$_2$-eNap wires is relatively weak, as also observed in the DOS diagrams. The most notable changes observed for the CH$_3$ heterojunction are a slight narrowing of the transmittance bands and a weak modulation of their intensities. In contrast, the position of the $T(E)$ peaks for eNap and Cl$_2$-eNap corresponds well to the position of their associated DOS peaks, and this is particularly clear for the three π-conduction bands near $-9.0$, $-7.5$, and $-6.6$ eV. Moreover, the large modulation of $T(E)$ calculated in the stacking direction suggests promising switching ability as the dispersion of individual bands in this triplet conduction band is approximately 300 meV, much larger than $kT$ or phonon frequencies. Although the presence of several states with comparable energies are revealed in DOS diagrams, the calculated $T(E)$ for the heterojunction does not indicate, for symmetry reasons, a significant overlap between conducting states. The difference in energy for the states in the first two bands above $E_F$ for eNap and Cl$_2$-eNap is sufficiently large to provoke the sharp decrease of the two corresponding $T(E)$ peaks in eNap(Cl$_2$)-eNap. Thus, we can expect strong backscattering of the carriers at the heterojunction interface, due to an absence of resonance between conducting states of individual segment. The first two bands that really contribute to the transport of carriers in the assembly appear at ±3 eV from $E_F$.

In conclusion, we have evaluated the electronic and charge transport properties of molecular assemblies made of two different 3,6-R$_{-1}$-ethyl-naphthalene ($R$:H, CH$_3$, Cl) fragments. We have shown that the presence of a CH$_3$ on eNap has a relatively weak influence upon the resulting electronic and transport properties of the systems. In contrast, the presence of Cl has a drastic effect on these properties, where strong carrier scattering is anticipated to occur near the interface. Finally, the electronic and charge transport properties of oligoassemblies can be tailored on a large ensemble of different π-electron rich molecular units (anthracene, tetracene, etc.) by modulating the donor-acceptor nature of functional groups.

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC), Ministère du Développement économique et régional et de la Recherche (MDERR), and Nano-Québec. The authors are grateful to the Réseau québécois de calcul haute performance (RQCHP) for providing computational facilities. One of the authors (P.B.) thanks NSERC, GCM, and École Polytechnique for financial support during this work. They also thank Arthur Yelon and Patrick Desjardins for their helpful comments on this letter.

10Hamiltonian and overlap matrix elements used for the evaluation of transmittance are determined using extended Hückel model (Ref. 13) with $s, p_x, p_y, p_z$ orbitals for C and Cl atom, and one $s$ orbital for each gold and hydrogen atom ($s$ orbitals dominate the DOS of gold near $E_F$).
15The calculated band gaps for periodic 1D eNap, (CH$_3$)$_2$-eNap and Cl$_2$-eNap are 2.68, 2.65, and 2.42 eV, respectively.
16Multilink population analysis of (CH$_3$)$_2$-eNap and Cl$_2$-eNap obtained from HP96-31G calculations revealed a decrease of electron charges on the naphthalene fragment by 0.24 e$^-$ and 0.16 e$^-$, respectively. In contrast, HOMO/LUMO levels are shifted by around ±0.15 and ±0.63 eV relative to $E_F$ of eNap for (CH$_3$)$_2$-eNap and Cl$_2$-eNap, respectively.

FIG. 3. Density of states (DOS) diagram (upper panels) and calculated transmittance (log$_{10}$[$T(E)$]) signals (lower panels) for ten unit assemblies of (a) eNap-(CH$_3$)$_2$-eNap and (b) eNap-Cl$_2$-eNap molecular units. The Fermi energy is indicated by the vertical dashed line, and the energies of HOMO and LUMO of the heterowires are identified by the arrows.