

Resonant Tunneling in Highly Organized Molecular Assembly

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The control of supramolecular architecture constitutes a major challenge in the development of high mobility organic semiconductor devices.¹ A promising class of organic materials exploits the stacking of conjugated polymers and molecules in which significant intermolecular π -electron coupling exists.² Different approaches for creating low-dimensional assemblies with tailored structural properties favoring π -stacking are emerging.³ One promising approach is self-directed assembly on a hydrogen-passivated Si(100) surface where molecular lines of styrene have already been created through a chain reaction growth mechanism. The main interest for this semiconducting surface is clearly the distance separating surface Si atoms (3.8 Å) on which the molecules are covalently attached which favors a significant π -electron coupling between molecules (see Figure 1).

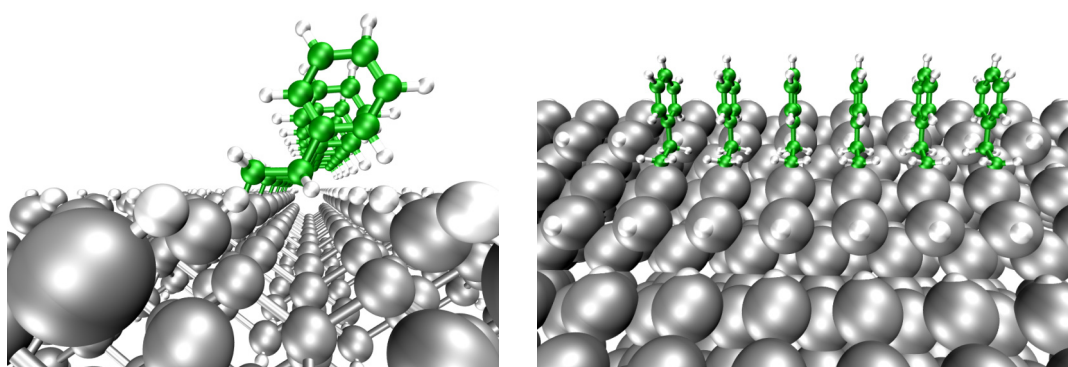


Figure 1. Formation of low-dimensional organic nanostructures on the reconstructed [2x1]Si(100) surface through a self-directed reaction.

The simplest and probably the richest existing molecular species to investigate fundamental aspects of π -stacking are small acenes such as naphthalene, anthracene, tetracene, and pentacene assemblies. Most of the previous experimental and theoretical studies on oligoacenes addressed issues related to the electronic structure and transport properties of very good or even perfect crystalline phases in which most of the molecules adopt a herringbone-like structure. Due to the relatively weak intermolecular π -electron coupling, these systems usually have a rather low mobility (10^{-6} - 10^{-2} cm²/ V s) and demonstrate relatively poor switching abilities. Recent interest for pentacene-based systems originates from the significant improvement in the production of good quality single crystals that give much higher mobility (0.1 - 10 cm²/ V s) than those of polycrystalline samples. In this presentation, we will present the results of tight-binding and DFT calculations on the electronic and electron transport properties of perfect π -stacked oligoacene wires that could possibly be synthesized on Si(100).

In a first attempt, we studied the variation of electronic properties of isolated acene-based molecules (benzene, naphthalene, anthracene, etc.) where the number of π -electron increases. Then, we investigated the variation of electronic and transport properties for the molecular species upon their assembling into a low dimensional nanostructure which mimics a self-directed assembly on the Si(100)[2x1] surface. On isolated molecules, we observed a drastic decrease of the band gap by more than 4.5 eV for acene molecules containing up to 15 members rings. An additional band gap decrease observed upon molecular assembling does not depend on the nature of the molecules but more on the separation between them. Oligoacene assemblies with intermolecular spacing $d_{\text{mol}} \leq 3.8 \text{ \AA}$ are characterized by improved π -electron coupling that facilitates the electrical transport through a resonant tunneling mechanism. For such molecular arrangement, we have computed significant band dispersion ($\approx 340 \text{ meV}$), high transmittance ($T(E) \sim 1$), and relatively high mobility for holes and electrons ($0.1\text{-}0.9 \text{ cm}^2/\text{Vs}$) in both resonant π -valence and π^* -conduction bands.

In a second effort, we have focused on the possibility to control the charge density of low energy π -electron in naphthalene-based molecule through a judicious choice of functional groups. We have considered the presence of methyl (CH_3) and chloride (Cl) groups for their donor-acceptor abilities. If one assumes that the charge density of π -electron can be modulated by functional groups, a mixture of two different functionalized molecules could, in principle, lead to the creation of a n-p molecular junction. Our results indicate that the most striking characteristic of this heterogeneous system is a partial localization of the frontier π -orbitals on either side of the molecular junction. The extent of the evanescent wavefunction 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 CH_3 -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.

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