Charge transfer in the TCNQ-sexithiophene complex

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Molecular crystals from thiophene molecules can be doped with TCNQ-F4 molecules for use in all-organic optoelectronic and semiconductor devices. The charge transfer and the molecular orbital energy level formation in between these two organic molecules are investigated here by density functional theory calculations. The isolated molecules are calculated nonbonded and bonded together, forming a charge transfer complex (CTC). The relaxed structure of the complex shows essentially coplanar and centered molecules with the α-sexithiophene rings tilted alternatingly by 4.8°. The bond formation of these molecules results in a charge transfer of ~0.4 e from the α-sexithiophene to the TCNQ-F4 molecule. The highest occupied molecular orbital–lowest unoccupied molecular orbital gap width is reduced as compared to the isolated molecules due to the newly formed orbitals in the CTC. Upon adsorption on a Au(111) surface, electrons are transferred onto the molecule complex, thereby causing the molecular levels to align asymmetric with respect to the charge neutrality level. The theoretical results for the single molecule and CTC layer are compared to experimental photoemission and scanning tunneling spectroscopy results. © 2008 American Institute of Physics. [DOI: 10.1063/1.2961014]

INTRODUCTION

Organic semiconducting molecular materials have promising electronic and optical qualities; light emission and devices based on their semiconducting properties are some of the applications. The structure of these molecular complexes, the design of energetic gaps, and the tailoring of the electronic properties by choosing appropriate ligands and counterparts can be investigated by theoretical calculations. A widely studied class of semiconducting polymers is based on oligothiophenes as donor: Here we used the α-sexithiophene (6T) molecule in conjunction with the 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQ-F4) molecule on the acceptor side. This charge transfer complex (CTC) system has potential applications as an organic semiconductor material and only some of its optical and electronic properties have been investigated by photoemission spectroscopy (PES), photo- and electroluminescence measurements, and recently by scanning tunneling spectroscopy (STS). A similar molecule pair, dimethylquaterthiophene and TCNQ-F4, has been investigated in a periodic crystal, while an x-ray absorption near edge spectroscopy study combined with density functional theory (DFT) calculations of the poly(3-hexylthiophene) and the TCNQ-F4 molecule couple was done for isolated molecules. The charge injection at the metal electrode plays an important role in devices but has been investigated to a lesser degree than for inorganic semiconductors. The individual molecules as well as the CTC have therefore been calculated adsorbed on a Au(111) surface. These conjugated molecules are physically adsorbed on the electrode material but still exhibit a substantial overlap of their orbitals with the electrode surface in order to supply a tunneling electron current. Our calculations have been performed for three different categories using ab initio principles. Isolated TCNQ-F4 and 6T molecules in the gas phase, the interacting TCNQ-F4-6T complex in the gas phase, and the molecules and CTC adsorbed on a surface slab.

For the calculation of the isolated molecules and the TCNQ-F4-6T complex in the gas phase, the molecular geometries were relaxed until total energy gradients were reduced below 1.0 meV/Å. For the adsorbed molecules, we used a Au(111) surface unit cell consisting of more than 200 atoms as the supporting substrate, the computational limits allowed here only for single energy point calculations. To assure robustness and accuracy of the results, local density approximation (LDA) and general gradient approximation (GGA) were used with different basis sets. All calculations are closed shell calculations in a singlet ground state.

ISOLATED MOLECULES

Figure 1 illustrates the relaxed structure of TCNQ-F4 and its first molecular orbitals. The molecule is rigid with a planar symmetry and has an inversion center. The structural parameters were calculated with LDA using a plane wave basis and the hybrid functional B3LYP using a 6-31G(d) atomic orbital basis set using ESPRESSO (Ref. 6) and GAMESS in the latter case. Throughout this manuscript unless stated differently, the basis for structural optimization will be 6-31G(d) and for the subsequent property evaluation, a 6-31G(p,d) basis set will be used. The interatomic distances appear to be unaffected by the choice of exchange and correlation functional and deviate by less than a few picometers. In contrast, the electronic structure of this molecule is more

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sensitive to the choice of the used method. The spectrum shown in Fig. 2 displays the discrete eigenvalues folded by a Gaussian with a width of 0.25 eV.\textsuperscript{8,9} LDA-DFT results in a larger highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap than the B3LYP-DFT spectrum from Fig. 2. Choosing a 6-31G($p,d$) basis set with PBE-GGA on the other hand yielded the same electronic structure as by choosing a plane wave basis set. Therefore, the B3LYP HOMO-LUMO gap amounts to 2.36 eV, while the single-particle gap, i.e., the difference between the electron affinity and the ionization potential, amounts to 5.26 eV. The calculated molecular electrostatic potential reveals that the fluorine atoms are more nucleophilic than the center atoms.

For the isolated 6T molecules, the relaxed structure was calculated again with B3LYP-DFT, LDA-DFT, and PBE-GGA using 6-31G($d$) and plane wave basis (cf. Fig. 3). The PBE functional and plane waves were also used in an all-electron calculation or together with pseudopotentials, resulting in only small changes in the electronic structure. For the 6T, the HOMO-LUMO B3LYP gap is determined as 2.61 eV while the single-particle gap amounts to 4.48 eV, see Fig. 4. Here, the gap width turned out to be unaffected from rotations of the thiophene rings. Substantial differences in the electronic structure between the atomic orbital basis and plane wave basis appear for the unoccupied states for energies above 3 eV only and are caused by the more delocalized character of these states as opposed to the localized character of the atomic orbital basis set. The molecule has no net dipole moment, although a single thiophene does have an in-plane dipole moment of 0.63 D. By rotating individual rings the net electric dipole moment of the 6T molecule can be tuned. The dipole moments for the bend structure with one rotated ring and the all-bend structure with five rotated rings using LDA and B3LYP are 1.0/1.1 and 1.8/2.0 D. The differences in total energy between the straight molecule and the molecule with one rotated ring are 52 and 63 meV using LDA and B3LYP, respectively. Higher differences in total energy are found for the 6T molecule with all rings rotated: 162 meV using LDA and 215 meV using B3LYP, thus an average of 30–60 meV increase in energy per rotation. These energy differences can still be activated at room temperature depending on the energy barrier to switch from one to another configuration.\textsuperscript{11}

**CHARGE TRANSFER COMPLEX**

In order to calculate the molecule interaction, the TCNQ-F\textsubscript{4} was initially placed above the thiophene molecule. Then, by gradually decreasing the distance between the molecules a potential minimum was finally achieved. Four symmetry inequivalent initial geometries were chosen by placing the TCNQ-F\textsubscript{4} centered either above a thiophene ring or above a thiophene-thiophene connection. The structures with the TCNQ-F\textsubscript{4} in the bridged geometries showed substantially lower energies than the ones centered above a thiophene ring and are therefore considered to be the preferential binding sites. The geometry with the TCNQ-F\textsubscript{4} in the center of the whole sexithiophene molecule reached the lowest energy.

The fully relaxed centered structure is shown in Fig. 5, which includes a few key characteristics: (1) The TCNQ-F\textsubscript{4} is adsorbed parallel at a medium distance of 3.4 Å; (2) its axis is aligned parallel to the carbon-carbon bond of the two underlying thiophene rings; (3) there is an alternating twist of the thiophene rings by 4.8° with the sulfur atoms pointing away from the TCNQ-F\textsubscript{4}; (4) the end rings are bent downwards, pointing away from the TCNQ-F\textsubscript{4}.

Both, LDA-DFT and GGA-DFT functionals were cho-
sen for the structural calculations and atomic orbitals were used. In the 6-31G basis, p and d shell polarization functions were added to take into account the weak delocalized interaction. A binding energy of $\sim 225$ meV corrected for the basis-set superposition error is determined, including contributions from the chemical bonding and electrostatic forces. Van der Waals interactions between the two molecules are not included since the used DFT functions do not describe them. They are expected to be small compared to the before mentioned contributions though.

We calculated the amount of charge transfer from the 6T to the TCNQ-F4 molecule. The LDA-DFT with a direct integration from a plane wave basis calculation gives an amount of 0.43 electrons that are transferred while a B3LYP-DFT calculation with 6-31G(p,d) atomic orbital basis using the charge decomposition analysis model\textsuperscript{12–14} provides an amount of transferred charge of 0.38 e. A rather large dipole moment of 5.3 D perpendicular to the molecules axis is determined, which is calculated by using the center of mass of the complex as origin.

The electronic structure from a B3LYP-DFT calculation is shown in Fig. 6. A gap width of 1.039 eV is determined. In the complex, new states have formed due to a substantial overlap of molecular orbitals from both fragments. The situation at the Fermi level is depicted in the fragment molecular orbital diagram of Fig. 7(a), which shows that the HOMO-LUMO gap of the complex is provided by the bonding and antibonding states resulting from the overlap of the 6T-HOMO-1 with the TCNQ-F4-LUMO-1. It is essentially these two molecular orbitals that participate in the charge transfer, as can be seen in Fig. 7(b) and 7(c). The newly formed CTC-HOMO-1 shows a stronger localization on the TCNQ-F4 in order to achieve transfer of the charge.
The spatial distribution of the electron density and the wave function of the HOMO-1 and the LUMO-1 of the complex can be seen from different perspectives in Fig. 5. The HOMO-1 is located on the thiophene while the LUMO-1 is located on the TCNQ.

Interestingly the formation of the electronic structure of the complex is not strongly dependent on the details of the structure—a density of states spectrum with the same general features can already be obtained with strictly parallel aligned molecules. On the other hand, molecules positioned side by side showed no attractive interaction.

**ADSORPTION ON Au(111)**

In this last part, we have calculated the individual 6T and TCNQ-F4 molecules adsorbed on a Au(111) surface as well as their CTC on the same surface. Figure 8 depicts the adsorption geometries and unit cells of the molecules and CTC adsorbed on one side of a Au(111) surface slab. The proposed orientations are based on recent experimental data using scanning tunneling microscopy. The adsorbed structures were kept fixed as determined from the gas phase. An electron donation into the molecule typically results in an upward motion of hydrogen atoms, which is omitted here since the binding occurs mainly via the sulfur atom. Additionally the cationic and the excited triplet state of thiophenes are planar, justifying the adsorption geometries used for calculation.

A four-layer Au(111) slab was used, showing practically a converged value of the surface energy with a bulklike density of states, while the electronic structure on the surface is

![Graph showing the electronic structure of the complete 6T-TCNQ-F4 complex](image1)

FIG. 6. (Color online) The electronic structure of the complete 6T-TCNQ-F4 complex (red) and projections on each fragment (blue and black). The HOMO-1 is located on the thiophene while the LUMO-1 is located on the TCNQ.

![Graph showing the fragment orbital method diagram](image2)

FIG. 7. (Color online) (a) The fragment orbital method diagram shows the constitution of the participating molecular compounds. Bringing the molecules together results in an overlap and formation of new molecular orbitals with a gap of 1.039 eV. (b) The same level formation is depicted also in the projected density of states line graphs (b) for the TCNQ-F4 and (c) for the 6T.
not expected to be fully developed yet. Only a Γ point was used in the calculation—as a trade-off between the computational cost and accuracy for the surface.

Both, single molecules and CTC are placed 2.7 Å above the surface, assuming physisorption of the molecules. A smaller distance was used than found for 1T molecules adsorbed on a Al$_{111}$ surface, where the authors consider adsorption by weak electrostatic forces due to a charge redistribution on the surface with the sulfur atom bound on top of the Au atom.

In Fig. 9(a) the projected densities of states for a TCNQ-F4 molecule in the vacuum phase and the one for being adsorbed on a Au(111) surface are shown. The HOMO-LUMO gap is reduced upon adsorption and the level alignment is shifted towards negative energies. This can be attributed to a charge transfer from the substrate to the molecule. In Fig. 9(b) the projected densities of states for the isolated and adsorbed 6T molecules are shown. The HOMO-LUMO gap here is also reduced but the position of the Fermi level remains unchanged. The results for the 6T on the slab reveal the intact low-lying valence levels followed by substantially broadened orbitals across the Fermi level. A detailed bond analysis for the case of the 6T molecule was done by projecting the free molecule wave function onto the molecule-slab wave function. A projection of the HOMO-1 and LUMO-1 showed that they hybridize essentially into unoccupied states around +4 eV.

For the CTC adsorbed on the surface, the projected densities of states are shown in Fig. 10. The topmost molecule, TCNQ-F4, shows a rigid shift in the spectral intensities to lower energies, indicating further charge transfer to the acceptor. The projected density of states of the 6T in the CTC has intact low-lying valence levels while the frontier orbitals are substantially broadened. The HOMO-LUMO gap is broadened. A pronounced rigid shift in the spectrum to lower energies upon adsorption displays charge transfer from the substrate into the 6T and to a lesser extent into the adsorbed molecule on top of it. Here the role of the 6T molecule changes and it becomes an acceptor as expected upon adsorption of a molecule pair with a strong vertical dipole moment pointing upwards.

**DISCUSSION**

We have systematically studied the molecular charge transfer between the electron donor-acceptor (6T-TCNQ-F4)
complex in two different environments—the gas phase and on the Au(111) surface. In order to extract the charge transfer information, the isolated molecules in the gas phase as well as on the Au(111) surface are calculated. The amount of transferred charge is directly expressed in the electronic structure. We therefore have calculated the density of states that is accessed in photoemission and STS experiments. By comparing experimental data with the calculations, one needs to consider whether the single-molecule metal interface can be regarded as (1) a more or less isolated molecule or (2) a molecule where the molecular orbitals are strongly hybridized with the substrate surface wave functions. In the former case the molecule becomes ionized and the transport gap results from the difference in anionic and cationic energies and the corresponding polarization energies of the surrounding medium; Frenkel excitons are created with the gap energy as the sum of the negative and positive polaron energies. We point out that the spectra calculated within the Mott model, i.e., in the gas phase, already yield reasonable information, the isolated molecules in the gas phase as well as on the Au(111) surface slab. A small shift in the otherwise unchanged spectrum is observed, indicating charge transfer onto the molecule. The projected frontier orbitals of the 6T molecule in the CTC adsorbed on the Au(111) surface slab are altered compared to the free CTC. The HOMO-LUMO gap width is reduced and extra gap states appear.

For monolayer coverage of molecules on metal substrates, hopping of localized charge carriers from and onto the molecule, taking into account the self-energy. We state here that in such a coherent tunneling picture can more adequately describe the involved processes since charge states have been observed rarely in a few cases. The measured HOMO-LUMO gap is therefore the optical gap as calculated here. Further evidence is given by a comparison between the STS and PES gap values with calculated single-particle gap values that amount to \( I-A = 5.26 \) eV for TCNQ-F4 and \( I-A = 4.48 \) eV for the 6T molecule. The PES gap values are evidently much smaller and amount to \( 1.70 \) eV for TCNQ-F4 and \( 2.52 \) eV for the 6T molecule; the same accounts for the STS spectra that yield gap values of 1.76 and 2.67 eV. The corresponding calculated values are 2.36 and 2.61 eV, respectively (Figs. 2 and 4). We attribute the residual difference between theory and experiment to multilayer adsorption and substrate roughness.

The transferred charge in the molecule complex has been calculated to be 0.4 electrons. This value compares well to a charge of 0.46 electrons, which has been derived for the charge transfer crystal of DMQtT and TCNQ-F4. Surprisingly, because the coordination of the molecules in such three-dimensional crystal structure is higher than that on the two-dimensional surface. Finally, the charge transfer has been investigated by subtracting the electron densities of the CTC from the individual 6T and TCNQ-F4 molecules. The spatial redistribution of the charge shows that not simply electron charge is added to the acceptor molecule but that the electron densities inside of the complete 6T and TCNQ-F4 molecules are organized anew.

In conclusion we have calculated the structural and electronic properties of the CTC system of TCNQ-F4 and 6T molecules. The optimized geometry of the weakly interacting molecules is determined, which shows twisting of the thiophene rings and a planar rigid TCNQ-F4. The charge transfer amounts to \( \sim 0.4 \) electrons and is altered upon adsorption on a Au(111) surface. There, the strong vertical dipole results in a charge donation into the CTC and out of the surface.

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A. A. Granovsky, PC GAMESS, version 7.0 (http://classic.chem.msu.su/gran/gamess/index.html)
S. Baroni et al., QUANTUM-ESPRESSO (see http://www.pwscf.org or http://www.pwscf.org).


S. I. Gorelsky, AOMIX, program for molecular orbital analysis, York University, Toronto, 1997 (http://www.sg-chem.net/).


