

Ab initio ultrafast dynamics in doped organic semiconductors

First-principles study of ultrafast charge-transfer dynamics in doped organic semiconductors

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In Short

- Calculate transient absorption spectra of laser-excited organic donor/acceptor interfaces
- Assess the role of solvents in the ultrafast dynamics of organic donor/acceptor interfaces
- Investigate the charge-transfer dynamics of organic semiconductors doped by Lewis acids and fullerene

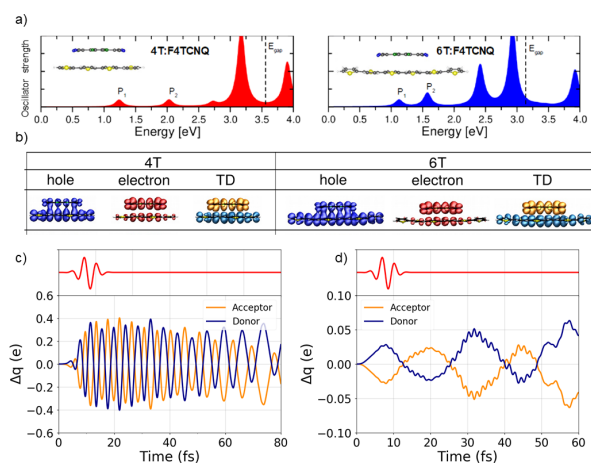


Figure 1: a) Optical absorption spectra of 4T/F4TCNQ and 6T-F4TCNQ interfaces 1. b) Hole, electron, and transition densities of the first bright excitations of both systems 1. c-d) Transferred charge from the donor to the acceptor in 4T/F4TCNQ with respect to the ground state at $t = 0$. The laser pulse, shown in the top panel, is in resonance with the excitation P_1 (c) and P_2 (d).

In project bep00076, we have been investigating the interfacial charge transfer of the 4T/F4TCNQ organic interface modeled an isolated dimer. This system is characterized by hybridized frontier orbitals with bonding and anti-bonding character 2. The first optical excitation P_1 , corresponding to the HOMO \rightarrow LUMO transition, is delocalized across the interface and polarized along the stacking direction 1. In the static regime, P_1 is classified as a Frenkel exciton in the charge-transfer (CT) complex, based on the spatial distribution of the electron and hole densities (see Fig. 1b) 1. To access the ultrafast CT dynamics at the 4T/F4TCNQ interface, we excite the system with a laser pulse in resonance with the energy of

P_1 and polarized in the stacking direction, allowing the nuclei to move according to the Ehrenfest dynamics. The dynamical charge transfer is monitored through the Bader charge analysis, partitioning the system between in the donor and the acceptor (see Fig. 1c). In the first few tens of fs after the impulsive perturbation, the charges distributed between 4T and F4TCNQ oscillate in anti-phase with an amplitude of about $0.4 e$ with respect to the reference value at $t = 0$. Considering that ground-state charge transfer is of the order of $0.5 e$, the application of the resonant pulse leads to an increase of CT which transiently approaches an integer charge. This result is particularly relevant considering that systems like the 4T/F4TCNQ interface are commonly addressed as CT complexes where only partial charge transfer occurs. This definition is based, however, on the analysis of their ground-state properties. In the dynamical regime this picture no longer holds true and further dedicated studies are needed to disclose the dominating physical processes in the ultrafast time window. In 1 we have shown that in the static regime the second bright excitation of 4T/F4TCNQ is polarized along the long molecular axis. However, the distribution of the electron and hole densities (see Fig. 1b) suggests a Frenkel-like character also for the second excitation P_2 . In order to understand whether these characteristics hold also in the dynamical framework, we have applied to 4T/F4TCNQ a laser pulse in resonance with P_2 , again releasing the nuclear motion. The first results of this new set of calculations, shown in Fig. 1d), indicate that in this case the dynamical CT is one order of magnitude lower compared to the one induced by the pulse in resonance with P_1 . We understand this behavior considering the polarization directions of the two excitations and, hence, of the two resonant pulses. The CT is maximized when the impinging photon is polarized along the stacking direction. As obvious as this finding may seem in retrospect, it is essential to verify its generality in order to rationalize the underpinning physical mechanism.

We quantified the amount of CT in the ground state between a polythiophene (PT) doped by the Lewis acid tris(pentafluorophenyl)borane (BCF). Modelling the donor by a 10T, periodically repeated in the chain direction, we find that a negligible CT of the order of $0.01 e$. This extremely electronic weak interaction is reflected by the density of states, where no hybridization between the species is visible (Fig. 2a). We also investigated related interfaces formed by 4T doped by BCF and also by BF_3 (an-

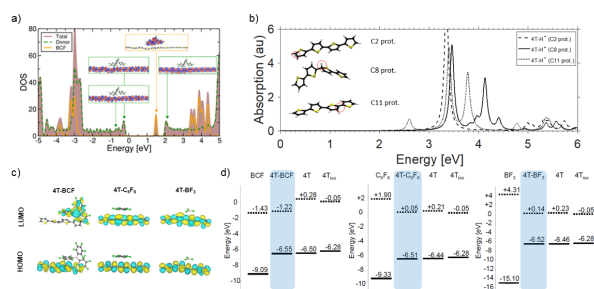


Figure 2: a) Density of states (DOS) of BCF-doped PT. b) Optical absorption spectra of protonated 4T molecules. c) Frontier orbitals and d) level alignment of 4T/BCF, 4T/HFB, and 4TBF₃ adducts. In panel d), the energies of the frontier states of isolated 4T (4T_{iso}) and of 4T in the geometry of the adducts are reported.

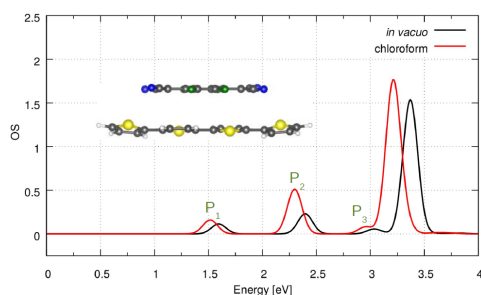


Figure 3: Optical absorption spectra of 4T/F4TCNQ computed from TDDFT in vacuo and in chloroform using the PCM model.

other Lewis acid) and by hexafluorobenzene (HFB), which are related to the building units of BCF. Also in these systems the ground-state CT is $\sim 0.01 e$ and the frontier states are not hybridized. However, in 4T/BF₃ and 4T/HFB, both frontier states are localized on the donor (see Fig. 2c). This behavior is clear from the type-II level alignment in 4T/BCF and the type-I in 4T/BF₃ and 4T/HFB.

The weak interaction between the donor and the acceptor in all these interfaces suggests that additional mechanisms are involved in the experimentally observed doping processes. Very recently it was proposed that protonation in solution can mediate the charge transfer from the donor to Lewis acids ³. To verify this hypothesis also in the case of oligothiophene, we have performed a set of calculations on protonated 4T in an effective solvent. These results indicate a significant dependence of the calculated spectrum on the protonation site, as shown in Fig. 2b). The observed behavior is driven by the fact that protonation breaks the conjugation of the 4T backbone. Hence, the spectrum of 4T protonated on the short edge is almost identical to the one of the pristine molecule, while 4T protonated in the middle of the molecular axis exhibit new optical signatures.

An important aspect regarding the doped organic semiconductors described above is the presence of the solvent. The protonation mechanism of 4T doped

by BCF occurs in an aqueous environment, where protons can effectively form through the dissociation of water molecules and subsequently interact with the donor. The linear absorption spectra reported in Fig 3b) are obtained treating the water solvent effectively through the polarizable continuum model (PCM). Now we aim at understanding whether the interaction with the solvent affects the charge transfer at the organic D/A interfaces. In preparation for this step, we have calculated the linear absorption spectrum of the 4T/F4TCNQ dimer in chloroform. As shown in Fig. 3, it is evident that the inclusion of an effective solvent induces an overall spectral red-shift due to the enhanced screening and also a redistribution of the oscillator strength.

In the continuation of this project, we aim to gain an in-depth understanding of the fundamental physical processes ruling charge transfer in doped organic semi-conductors. In addition to the role of vibronic coupling, we also want to assess the effect of a solvent embedding the laser-excited system. The calculations performed in the continuation of this project will contribute to the preparatory work of a DFG proposal focused on interfacial charge transfer in organic D/A interfaces including different electron-withdrawing species, such as Lewis acids and fullerene acceptors. All calculations will be carried out with OCTOPUS, an open-source code that offers an efficient parallel implementation of RT-TDDFT supercomputing architectures. This package offers all the features that are necessary to accomplish the proposed tasks, including an efficient implementation of the Ehrenfest dynamics ⁴ and of the formalism to compute laser-driven transient absorption spectroscopy and ultrafast dynamics ⁵. An implementation of the PCM was recently included ⁶.

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More Information

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