

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

- Ultrafast charge-carrier dynamics in doped organic semiconductors
- Role of electron-vibrational coupling in the charge-transfer dynamics
- *Ab initio* formalism based on real-time time-dependent DFT

Doping in organic semiconductors is a ubiquitous phenomenon appearing when donor and acceptor molecules are combined together. It critically determines the electronic, optical, and transport properties of the resulting materials ¹. Two main mechanisms have been identified to be responsible for doping in organic semiconductors: Integer charge transfer (ICT) manifests itself with an electron being transferred from the donor to the acceptor leading to the formation of ion pairs. Partial charge transfer occurs upon electronic hybridization of the frontier orbitals of the donor and the acceptor, giving rise to a charge-transfer complex (CTC). Recent experimental observations have drawn the attention on the role of conjugation length in the donor species doped by molecular acceptors ²: ICT is observed when the strong electron acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F4TCNQ) is blended with the poly-3-hexylthiophene (P3HT) polymer while a CTC is formed by the quarterthiophene oligomer doped by the same molecule. On the way to address this problem in its general complexity, we recently clarified the role of the donor conjugation length on the electronic structure of CTCs formed by oligothiophenes (nT) of increasing length ($n = 4, 6, 8, 10$) doped by F4TCNQ (see Fig. 1).

We performed a systematic analysis of the electronic structure and optical excitations in these systems by means of density-functional theory (DFT), adopting the range-separated hybrid functional CAM-B3LYP ³, and many-body perturbation theory (MBPT), including GW and the Bethe-Salpeter equation ⁴. The frontier orbitals of the individual components display a type-II level alignment, with the LUMO of the acceptor comprised between the HOMO and the LUMO of the donor (see Figs. 2a-d, black lines). However, the frontier levels of the CTCs do not reflect this alignment but display pronounced bonding and anti-bonding character which

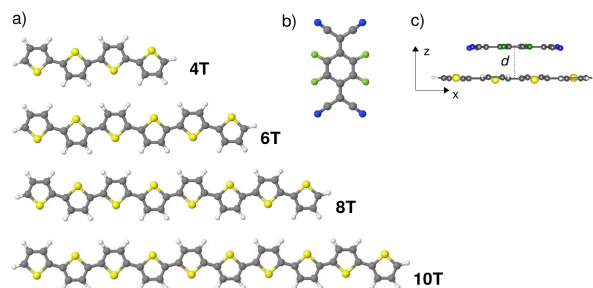


Figure 1: Ball and stick representation of the systems investigated in this project. a) Oligothiophene molecules with increasing number of rings ranging from 4 to 10. b) 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) molecule used as electron acceptor. c) Side view of the do-nor/acceptor complex 4T/F4TCNQ.

is a signature of enhanced hybridization. Upon increasing donor length, the size of the electronic gaps, given by the difference between the LUMO and the HOMO of the CTCs, decreases monotonically. Interestingly, this trend is mainly determined by the upshift of the HOMO, while the energy of the LUMO remains almost constant in all complexes. The optical properties of the CTCs, summarized in Fig. 2e), reveal that the optical gap of all systems (P_1), corresponding to the transitions from the HOMO to the LUMO, remains almost at the same energy regardless of the donor length. The second bright excitation P_2 , which arises from the transition from the HOMO-1 to the LUMO shifts to lower energies at increasing nT length. These two excitations have the same character in 4T/F4TCNQ, with the electron and hole both localized within the whole CTC. On the contrary, in the dimers with longer nT chains, P_2 becomes more remarkably charge-transfer-like, with the hole (electron) mainly localized on the donor (acceptor) side of the dimer.

These findings stimulate the interest in a deeper investigation of the dynamics of charge-transfer at the interface between these donor/acceptor complexes. Since such problems are out of reach for MBPT in realistic systems like the CTCs investigated here, we will rely in this study on real-time time-dependent DFT (RT-TDDFT) which offers the optimal trade-off between accuracy, feasibility, and physical insight. In this formalism it is possible to simulate pump-probe experiments, following the dynamics of the electronic system in the presence of an external laser pulse evolving with it. By exciting the systems with a monochromatic femtosecond (fs) laser pulse, we will follow the dynamics of the photo-excited electronic population in the sub-picosecond timescale

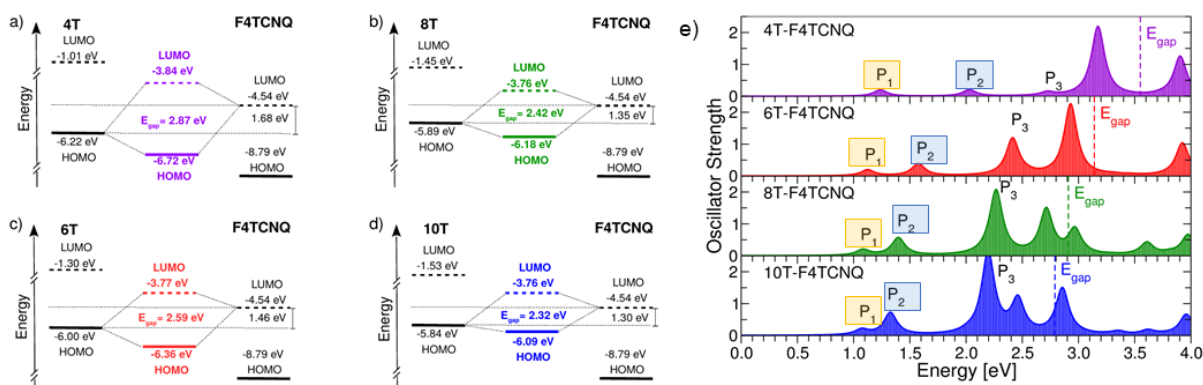


Figure 2: Electronic and optical properties of the absorption spectra of the $nT/F4TCNQ$ ($n=4,6,8,10$) complexes. a)-d) Energy level alignment computed from DFT with the CAM-B3LYP functional for the dimers and their individual components. e) Optical spectra computed from GW-BSE: The first three bright peaks are labeled as P_1 , P_2 , and P_3 , and the energy of the electronic gaps is indicated by dashed vertical lines.

and calculate the corresponding transient absorption spectra (TAS). The frequency of the applied pulse will be set in resonance with the energy of the two lowest-energy excitations in all complexes (P_1 and P_2 , highlighted in Fig. 2e). As discussed above, these two excitations have a different composition in terms of single-particle transitions and, most importantly, exhibit a different character upon increasing donor length 5. It is therefore relevant to understand whether the charge-transfer dynamics associated to these two excitations gives rise to different behaviors. In this analysis we will also assess the role of vibrational modes that coherently mediate the charge-transfer process. This mechanism was shown to play a crucial role in the ultrafast charge transfer in polythiophene/fullerene blends 6. For this purpose, we will performed coupled electron-nuclear dynamics according to the Ehrenfest scheme.

Calculations will be carried out with OCTOPUS 7, 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 8 and of the formalism to compute laser-driven transient absorption spectroscopy and ultrafast dynamics 9.

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<https://www.physik.hu-berlin.de/en/eos>

More Information

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