Molecular doping of PCPDT-BT copolymers: comparison of molecular complexes with and without integer charge transfer

Chuan-Ding Dong and Stefan Schumacher

1Department of Physics and Center for Optoelectronics and Photonics Paderborn (CeOPP), Paderborn University, Warburger Strasse 100, 33098 Paderborn, Germany
2College of Optical Sciences, University of Arizona, Tucson, AZ 85721, USA

Molecular doping in conjugated polymers is a crucial process for their application in organic photovoltaics and optoelectronics. In the present work we theoretically investigate p-type molecular doping in a series of (poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b”]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDT-BT) conjugated oligomers with different lengths and three widely-used dopants with different electron affinities, namely F4TCNQ, F6TCNNQ, and CN6-CP.

We study in detail the molecular geometry of possible oligomer-dopant complexes and its influence on the doping mechanisms and electronic system properties. We find that the mechanisms of doping and charge transfer observed sensitively depend on the specific geometry of the oligomer-dopant complexes. For a given complex different geometries may exist, some of which show transfer of an entire electron from the oligomer chain onto the dopant molecule resulting in an integer-charge transfer complex, leaving the system in a ground state with broken spin symmetry. In other geometries merely hybridization of oligomer and dopant frontier orbitals occurs with partial charge transfer but spin-symmetric ground state. Considering the resulting electronic density of states both cases may well contribute to an increased electrical conductivity of corresponding film samples while the underlying physical mechanisms are entirely different.

INTRODUCTION

With an increasing demand for applications based on organic semiconductors (OSC) such as light-emitting devices, transistors, and organic photovoltaics, of major interest is the enhancement of the OSCs’ conductivity by molecular doping [1–3]. P-type doping is typically achieved by admixing small acceptor molecules with a high electron affinity into the OSC matrix which was shown to increase the conductivity of conjugated polymer films up to orders of magnitude [3–6]. The interaction between the dopant molecules and the polymer chains is at the heart of the doping process, for which the underlying microscopic mechanism are quite complex. Two physically different pictures are regularly reported, (i) integer charge transfer (ICT) between the OSC and the dopant and (ii) hybridization of the frontier molecular orbitals of the two parties [7, 8]. As schematically illustrated in Figure 1, in the case of ICT one electron is transferred from the HOMO of the OSC to the lower-lying LUMO of the dopant, resulting in a singly positively charged polymer chain on which a polaron is formed and a negatively charged dopant molecule. This mechanism leads to a complex with a positively charged polaron on the oligomer chain and a negative charge on the dopant. This mechanism leads to a complex with a positively charged polaron on the oligomer chain and a negative charge on the dopant. In contrast to this, the HOMO of the OSC and the LUMO of the dopant can also hybridize and form bonding- and anti-bonding type orbitals, leading to a partial charge transfer. In experiment, these two mechanisms can be distinguished using optical spectroscopy, as the electronic excitations are qualitatively different and free charges on the polymer chains show up as distinct polaron absorption features [9–14]. Also different vibrational modes exist with unique optical fingerprints in the infrared spectral range [15–19]. In conductivity measurements generally only a limited fraction of the doping-induced positive charges contributes to the electric current, as many of them remain Coulombically bound and localized in the polymer-dopant ionic complexes [7].

Going more into detail, the relatively simple picture based on single-particle energy levels illustrated in Fig. 1 and widely discussed in the literature is known to be oversimplified [20]. Sometimes ICT is also found in complexes in which the HOMO of the OSC is only close to but still lower in energy than the dopant LUMO [3, 9, 20], and an ICT-based two-step picture relying on energetic...
disorder of the resulting ion pairs is proposed [21]. On the other hand, even when the OSC HOMO is higher in energy than the dopant’s LUMO, sometimes only formation of charge transfer complexes by hybridization of frontier orbitals is reported [10, 22, 23]. A more detailed review is given in Ref. [8, 9]. To further clarify the underlying mechanisms also the host dependence of specific dopant electron affinities was discussed [24] and doping in ordered molecular films with different morphologies [25]. Also double doping with a single small dopant molecule was recently observed experimentally [26]. In addition to the energetic pictures, also the influence of inter-molecular geometrical aspects on the doping mechanisms has been discussed [18].

In light of the increasing interest to also understand the microscopic origins in mixed conjugated polymer and dopant systems, in the present study we investigate p-type doping for a series of PCPDT-BT oligomers with different lengths and three dopants with different electron affinities. We explicitly study oligomer-dopant complexes such that the influence of the remaining counter ion is included, which is often neglected in theoretical studies. Our study confirms established trends that are expected from a single particle energy level point of view. As such we find that doping is more easily achieved in the longer oligomers where the oligomer HOMO is higher in energy compared to the dopants’ LUMO. Also doping is easier to achieve with increasing electron affinity from F6TCNNQ over F4TCNQ to CN6-CP, with the latter being the strongest dopant in the present study. More intriguingly, however, computationally exploring the geometries of different oligomer-dopant complexes on a molecular level, we also find a subtle dependence of the doping mechanisms at work on details of the geometry of the oligomer-dopant molecular complex that forms. For identical constituents we often find different stable equilibrium geometries some of which show ICT and some of which only hybrid orbital formation.

**SYSTEMS AND COMPUTATIONAL METHODS**

The PCPDT-BT oligomers studied in this work contain 3 (trimer), 5 (pentamer), and 7 (heptamer) alternating donor and acceptor units, respectively. The dopant molecules considered are F4TCNQ, F6TCNNQ, and CN6-CP. The molecular structures of the oligomers and the dopants are shown in Figure 2. To reduce the computational effort in our model study, the long side chains on the oligomers are replaced by methyl groups. We note that this only has a negligible effect on the behaviour of the frontier molecular orbitals and on their energetics which are most relevant in the present work. Below we study different molecular complexes each based on one of the oligomers and one dopant molecule. For each combination of oligomer and dopant molecules the geometry of the entire complex is optimized in the electronic ground state based on density functional theory. After the optimization the system is either found in an electronic state with spin-symmetry breaking for which an electron was transferred from the oligomer to the dopant molecule (integer charge transfer) or in an electronic state where merely orbital hybridization between oligomer and dopant has occurred but spin symmetry remains intact.

In the density functional theory formalism, the mechanism of integer-charge transfer illustrated in Figure 1(a) is manifested in the spatial localization of a pair of $\alpha$ and $\beta$ Kohn-Sham orbitals on different parties of the complex. This marks a broken spin-symmetry and naturally requires separate treatment of the two spin channels. To this end spin-unrestricted calculations were adopted to allow spin-symmetry breaking, and with ICT, in the electronic ground state of the complexes studied. The electronic structure calculations were initialized by mixing the HOMO and LUMO orbitals which serves as a seed to break the spatial symmetry of $\alpha$ and $\beta$ electrons.

Following our previous work [18], to account for long-range charge-transfer effects we use the unrestricted cam-B3LYP functional and 6-31G** basis set unless otherwise noted. Dispersion interaction is taken into account using Grimme’s D3 scheme with Becke-Johnson damping function to account for van-der-Waals interaction. All calculations were performed using the GAUSSIAN09 software package [28]. In some cases in order to analyze the charge transfer mechanism further, we also calculated the electronic states of the individual oligomer and dopant molecules in the fixed geometries they assume in the molecular complexes (used in Figure 7). Spin restricted calculations were performed to single out the structural effect of the ICT geometry on the electronic structure.
TABLE I. Summary of results for charge transfer in the optimized oligomer/dopant complexes studied. A and D indicate different positions of the dopant molecules, facing acceptor (BT) or donor (CPDT) unit of the oligomer chain, respectively. "Yes" indicates the occurrence of integer charge transfer (ICT) with spin symmetry breaking in the electronic ground state, "No" indicates a spin symmetric electronic ground state without ICT and formation of a charge-transfer complex with some orbital hybridization. For each oligomer/dopant complex, the charge transferred from the oligomer chain onto the dopant molecule calculated by Hirshfeld’s scheme is given in brackets. For complexes where stable structures were found for both ICT and non-ICT, the asterics symbol (*) marks the complex with lower total energy.

|           | trimer | pentamer          | heptamer        |
|-----------|--------|-------------------|-----------------|
| F4TCNQ A  | No (0.11) | A: No (0.30) | A: Yes (0.70) |
| D: No (0.27) |        | D: Yes (0.80)/No* (0.29) | D: Yes (0.78)/No* (0.18) |
| F6TCNNQ A  | No (0.16) | A: No (0.21) | A: Yes (0.71) |
| D: No (0.09) |        | D: Yes (0.80)/No* (0.17) | D: Yes* (0.83)/No (0.21) |
| CN6-CP A   | Yes* (0.87)/No (0.44) | A: Yes (0.78) | A: Yes (0.78) |
|           | D: Yes (0.84) | D: Yes* (0.85)/No (0.44) | D: Yes (0.86) |

of the complexes (used in Figure 8). We note that although the cam-B3LYP functional with dispersion correction gives a sensible relative ordering of energy levels from which useful physical pictures of the processes studied can be derived, absolute values of energies stated usually do not compare favourably with their experimentally determined counterparts. The Hirshfeld charges given in Table I and the density of states in Figure 3, Figure 4, and Figure 8 were prepared using the software Multiwfn [29].

RESULTS AND DISCUSSION

For each molecular complex consisting of oligomer and dopant, we distinguish two different positions of the dopant molecule with respect to the oligomer chain, namely the dopant either facing a donor unit or an acceptor unit of the oligomer. In addition to this qualitatively different positioning of the dopant molecules, geometry optimization was started from a number of different initial geometries differing in structural details of the constituents and/or their relative orientations. This way, for some complexes different local minima in the potential energy landscape were found showing different doping behaviour. For each of these optimized geometries, the electronic ground state was inspected as to its nature in terms of spin symmetry. A scenario in which a charge transfer from the oligomer chain onto the dopant, thus the occurrence of integer charge transfer (ICT), is easily identified by a broken spin symmetry in the electronic ground state which we find to be typically accompanied by a net charge transfer of more than 0.7 e. Table I summarises the calculated results for a representative selection of complexes studied. A general observation is that, while the ICT takes place in all the complexes containing CN6-CP and/or the heptamer (regardless of the position of the dopant) it is not always found in the other complexes. This finding confirms earlier findings [30] where CN6-CP was identified as the strongest molecular dopant among the series of dopants studied in the present work. Although alignment of single-particle energy levels is recognized not to be the only driving factor for ICT to occur [20], the strong doping strength of CN6-CP is also reflected by its lower LUMO level [27].
The existence of electronic configurations showing either ICT or non-ICT for identical molecular complexes but only slightly different geometries, naturally motivates a more detailed comparison. Take as a first example the pentamer/CN6-CP(D) complex. Figure 3 shows the partial density of states (PDOS) for the two optimized structures with and without ICT, respectively. The PDOS is calculated by projecting the calculated global molecular orbitals onto the atomic orbitals belonging to each of the two molecules in the complex. The ICT between the pentamer and CN6-CP (upper left panel of Figure 3) is manifested in the broken spin symmetry as well as in the spatial localization of for example α-HOMO and β-HOMO on the CN6-CP and the pentamer, respectively. The α-LUMO orbital can be interpreted as the missing electron or "hole" on the oligomer chain after ICT occurs. This state lies significantly higher in energy than the highest occupied state of the bare oligomer chain (for comparison the latter is included as the bottom right panel of Figure 3). A relatively high activation energy may be needed for this state to function as a mobile charge carrier and increase the system’s electrical conductivity. The close proximity to the doping-induced excess negative charge on the dopant shifts the induced positive charge on the oligomer upwards in energy compared to an individual pentamer chain with an extra positive charge as shown in the top right panel of Figure 3. As shown in the lower left panel of Figure 3, in the pentamer/CN6-CP(D) complex without ICT spin-symmetry is preserved. Only a low degree of hybridization of the pentamer’s HOMO and the CN6-CP’s LUMO orbitals is observed. As shown by the PDOS, the empty in-gap state at about -4.0 eV, introduced by the hybridized LUMO, is around 2.0 eV higher than the HOMO state. This energy separation is significantly lower than in the case of ICT. Thus arguing based on the density of states, although no ICT is achieved here, a partial electron vacancy is created on the oligomer chain which in an extended film sample may well contribute to increase the system’s conductivity. We further note that consistent with our previous findings [18], as a general trend we find that ICT appears to be more easily achieved when the dopant molecule is positioned in front of the donor unit of the oligomer chain and the amount of total charge transferred is also typically higher in that case once ICT has occurred.

We obtain qualitatively similar results for the heptamer/F6TCNNQ complex with and without ICT as discussed above for the pentamer/CN6-CP complexes. Results for heptamer/F6TCNNQ complexes are shown in Figure 4. For the ICT case, due to the slightly longer chain length, on the heptamer site the α-LUMO state (the doping-induced “hole” on the oligomer chain) lies a bit closer (compared to the pentamer case) in energy to the highest occupied state in the bare oligomer. For the non-ICT case only a less pronounced hybridization between heptamer HOMO and F6TCNNQ LUMO is ob-

FIG. 4. Same as Figure 3 but for heptamer/F6TCNNQ complexes. Top left panel shows density of states for the ICT complex with spin-symmetry breaking and bottom left panel for the non-ICT complex. Panels on the right for comparison density of states for neutral heptamer and heptamer with an extra positive charge.

than those of F4TCNQ and F6TCNNQ. In addition, the results confirm that the longer the oligomer chain, the less the oligomer HOMO level is shifted downwards in energy by quantum-confinement between the chain ends, and the more energetically favourable the ICT becomes.

For many of the complexes showing ICT, we also find one or more alternative optimized structures without ICT (the "No" cases in Table1). In other words, for the same molecular complexes, both the possibilities of ICT and non-ICT exist [17], which correspond to different local minimum structures. The results show that the optimized ICT structures can be energetically more favourable or less favourable than those without ICT. We note that energy differences typically are bigger than thermal energies and are on the order of 100 meV to 1 eV per complex. However, we reckon that in disordered doped oligomer films with possible additional ‘external’ geometry constraints to the molecular constituents’ geometries imposed by the real side chains or local film environment, different complex geometries are expected to be realized to some extent. In the present work we restrict the discussion of geometries for a few representative cases for the purpose of understanding ICT and partial charge transfer and do not attempt to perform a complete screening of all possible geometries.
FIG. 5. Isosurfaces of selected HOMO and LUMO orbitals of the ICT complexes for α and β electrons (isovalue=0.004). Comparison of α HOMO (electron transferred onto dopant) and α LUMO orbitals (remaining electron vacancy on the oligomer, i.e., a positively charged polaron) of the ICT complex illustrates the integer charge transfer process. Breaking of spin symmetry is illustrated by comparing for example α HOMO (localized on the dopant) on the left and β HOMO (localized on the oligomer) in the panel on the right. Frontier orbitals of the non-ICT complex (not shown here) only show a relatively small degree of hybridization but more importantly remain spin-symmetric.

served leading to an only very small density of electron vacancies on the oligomer inside the gap. Some lower-lying states, e.g. the states between -7.0 eV and -8.0 eV, show a more pronounced hybridization as the original orbitals of the bare constituents are closer to resonance with each other.

In addition to the PDOS discussed above, for the ICT case, in Figure 5 we show examples for the HOMO orbitals in the two spin channels for both complexes, pentamer/CN6-CP and heptamer/F6TCNNQ. For each complex, comparing α-HOMO (transferred electron localized on the dopant) and α-LUMO (missing electron or "hole" localized on the oligomer) the charge transfer from oligomer chain to dopant is apparent. Comparing for example α-HOMO and β-HOMO, the spin symmetry breaking is also clearly visible as these two orbitals are spatially localized on different entities of the complexes. Finally we would like to reiterate that we ran geometry optimizations for several initial geometries out of which only representative optimized structures are explicitly discussed here. Furthermore we did not attempt to find or explore all the possible stable local minima on the potential energy surface in the present work. Therefore, also for the molecular complexes with (e.g. heptamer/CN6-CP A in Table I ) or without (e.g. trimer/F4TCNQ A and D in Table I) ICT, the other possibility should not be fully ruled out but would not add anything fundamentally new to the present discussion.

To shed some additional light on the dopant-induced changes induced to the carbon-carbon bonding in the oligomers, in Fig. 6 we show examples for the change of C-C bond lengths along the oligomer backbones in structures with and without ICT. Bond lengths are measured relative to the carbon-carbon bonds in the corresponding isolated and neutral oligomers. For the ICT case, change in bond lengths is located in the spatial region where the excess positive charge (polaron) is located and extends for about 5 donor/acceptor units and becomes less significant when close to both ends. Also compare with the isosurfaces of the α-LUMO orbitals shown in Figure 5. Comparing with the non-ICT case, we note that also the partial charge transfer due to hybridization of frontier orbitals gives rise to a localized alternation of carbon-carbon bonds, however, with a reduced magnitude.

In the simplest single-particle energy level picture,
the widely-discussed mechanism of ICT, electron transfer from oligomer to dopant, would require a positive HOMO\textsubscript{polymer}-LUMO\textsubscript{dopant} energy offset (as illustrated in Figure 1(a)). However, in a more complete electronic picture this may not be required as electronic correlations can also play an important role as a driving mechanism for ICT to occur [20].

The situation becomes even more complex when changes in the molecular geometry after ICT has occurred are taken into the discussion. At an attempt to partly disentangle these different contributions, as a first step we compare the HOMO of the oligomer and the LUMO of the dopant, each calculated from the respective isolated molecules’ equilibrium geometries with the corresponding energies obtained from the fixed geometries in the ICT and non-ICT complexes.

To obtain the latter, oligomer and dopant, respectively, were removed after complex geometry optimization and single point calculations where performed for the remaining molecule. Compared to the optimized geometry of the isolated oligomer molecules a number of structural changes occur when a complex with the dopant molecule is formed. Most prominently these include a bending of the entire chain. Another important change is the change of the bond length as a consequence of excess positive charge on the oligomer discussed above. In particular the change of the bond length significantly influences the energies of single particle levels on the oligomer chain. This effect can be singled out when calculating the energy levels in the charge neutral state of the oligomer in the geometry obtained by optimizing with an extra positive charge (dashed horizontal line in Figure 7).

Compared with the geometries of the individual isolated molecules (see Figure 7(a)), the oligomers in both the ICT and non-ICT complexes have their HOMO level shifted upwards in energy. For the LUMO levels in the dopant molecules we find this situation in reverse. All shifts are more pronounced in the ICT case than in the non-ICT case. Additionally comparing the HOMO shifts in the oligomers with the HOMO energies calculated for the polaron geometry, one can see clearly that the upward shifts of the HOMO energies are predominantly caused by the alternation of carbon-carbon bonds in the presence of an extra charge. Therefore the upward shift of HOMO energies on the oligomers in the ICT complex should be interpreted as a consequence of, rather than the cause of the ICT. We note that even with the up-shifted HOMOs of the oligomers, the HOMO\textsubscript{polymer}-LUMO\textsubscript{dopant} offset is still far (particularly in the heptamer/F6TCNNQ complex) from being positive. And still, for certain geometries, ICT is observed. These results once more illustrate [9, 20, 27] that the interpretation of ICT based on single-electron energy levels is not sufficient but detailed calculations for relevant oligomer/dopant complex structures are needed.

We would also like to analyze the effect that the different geometries of ICT complexes and non-ICT complexes for the same molecular constituents have on the hybridization of molecular orbitals. A direct comparison of electronic properties of the ICT structure and the non-ICT structure can only be done using a spin restricted computational approach for both geometries. To this end, we performed single point spin restricted calculations for the ICT and non-ICT structures of the heptamer/F6TCNNQ complex as an example (the same molecular structures are used as in Figure 4). As shown in Figure 8, with the restricted spin symmetry, the ICT structure leads to a significantly enhanced hybridization between the heptamer’s HOMO and F6TCNNQ’s LUMO, which is also in agreement with the hybridization picture presented in Figure 1(b). Electronically, the enhanced hybridization of the frontier orbitals can be seen as a precursor for the ICT such that actual ICT can occur once the restriction of spin symmetry is lifted.

![FIG. 7. Comparison of molecular orbital energies (in electron Volts) of the individual constituents in the complexes studied. Left panels give energies of orbitals on the oligomer, right panels give energies for orbitals on the dopant. (a) Calculated pentamer HOMO and CN6-CP LUMO energies for different molecular geometries in the charge-neutral state. Solid black: energy for a geometry optimized for an individual neutral molecule. Red: energy for a geometry optimized for the ICT complex but with dopant (left) or oligomer (right) removed after optimization. Green: energy for a geometry optimized for the ICT complex but with dopant (left) or oligomer (right) removed. Dashed black: the HOMO energy of the neutral oligomer in the geometry that was optimized with an extra positive charge (polaron geometry). (b) same as (a) but for heptamer and F6TCNNQ. (a) and (b) As absolute values are not relevant to the processes discussed, in each panel energies are given relative to the HOMO of the respective neutral oligomer (black lines).](image-url)
find that specifics of the molecular geometry in which a certain oligomer-dopant complex forms can be decisive in whether integer charge transfer may occur or not. Details may include the relative positioning of the dopant to the co-polymer chain as discussed previously [18] but even more so for the examples studied here, different stable geometries often exist. Those are likely to be realized in film systems where additional external constraints are naturally present for each complex in the system. For the same composition of oligomer-dopant complexes in some geometries these show ICT and in others they do not.

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CONCLUSIONS

In this work we investigated the p-type doping in a series of molecular complexes containing PCPD-T-BT oligomers of different lengths (trimer, pentamer, and heptamer) and different dopant molecules (F4TCNQ, F6TCNQN, and CN6-CP). In particular we focus on the possibilities of integer-charge transfer, where an entire electron is transferred from the oligomer chain onto the dopant molecule such that the complex is in a ground state with broken spin-symmetry, and compare this with cases where some transfer of charge occurs but due to the formation of hybrid orbitals between oligomer and dopant frontier orbitals. In general, our results emphasize that merely looking at the oligomer and dopant molecular orbital energies only certain trends in the doping behaviour can be understood, however, single-particle energetics is not enough to understand whether doping occurs and with which mechanism. On a molecular orbital energy level we can understand that doping gets easier the longer the oligomer chain leading to a more favourable alignment of frontier orbitals due to the reduced quantum confinement. Also electron affinity of the dopant, here increasing from F6TCNQN to F4TCNQ to CN-6CP can generally be understood from the LUMO energies in these dopants. For further details, however, full calculations of polymer-dopant complexes are needed that in particular allow for breaking of the spin-symmetry in the electronic ground state. From such calculations we

FIG. 8. Density of states from spin-restricted calculations for ICT (left) and non-ICT structures (right) of the heptamer F6TCNNQ complex. Using a spin-restricted formalism, in the panel on the left spin-symmetry breaking is suppressed compared to the upper panel of Figure 4. In the panel on the right, the data coincides with data shown in the lower panel of Figure 4, where spin-symmetry is preserved also in the spin-unrestricted calculation. Only small differences are seen in the two panels resulting from the slightly different geometries. The most apparent change is the slight reduction in the HOMO-LUMO gap due to difference in bond length alternation in the ICT and non-ICT structures (cf. Fig. 6).

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