On the relation between local and charge-transfer exciton binding energies in organic photovoltaic materials

Hilde D. de Gier\textsuperscript{a}, Ria Broer\textsuperscript{a}, Remco W.A. Havenith\textsuperscript{a,b}

\textsuperscript{a}Theoretical Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands; \textsuperscript{b}Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands and Ghent Quantum Chemistry Group, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281, B-9000 Gent, Belgium

ABSTRACT

In organic photovoltaic devices two types of excitons can be generated for which different binding energies can be defined: the binding energy of the local exciton generated immediately after light absorption on the polymer and the binding energy of the charge-transfer exciton generated through the electron transfer from polymer to PCBM. Lowering these two binding energies is expected to improve the efficiency of the devices. Using (time-dependent) density functional theory, we studied whether a relation exists between the two different binding energies. For a series of related co-monomers, we found that the local exciton binding energy on a monomer is not directly related to that of the charge-transfer exciton on a monomer-PCBM complex because the variation in exciton binding energy depends mainly on the variation in electron affinity, which does not affect in a direct way the charge-transfer exciton binding energy. Furthermore, for the studied co-monomers and their corresponding trimers, we provide detailed information on the amount of charge transfer upon excitation and on the charge transfer excitation length. This detailed study of the excitation process reveals that the thiophene unit that links the donor and acceptor fragments of the co-monomer actively participates in the charge transfer process.

Keywords: organic photovoltaics, (time-dependent) density functional theory, donor-acceptor co-monomers, local exciton, charge-transfer exciton, exciton binding energy

1. INTRODUCTION

Solar energy is an attractive renewable energy source for which effective and low-cost solar cells are needed. Currently, silicon-based photovoltaic (PV) devices are the most common solar cells because of their high power-conversion efficiency (PCE) of 20-25\%\textsuperscript{1}. Unfortunately, their production process requires many steps, uses large amounts of toxic chemicals, is energy consuming and expensive.\textsuperscript{2} An appealing alternative is the organic photovoltaic (OPV) device. This type of solar cell has several advantages compared to silicon-based PV devices: it can be produced from cheap and abundant materials using low-cost (\emph{i.e.}, solution-processing) and large-scale fabrication methods (\emph{e.g.}, roll-to-roll printing).\textsuperscript{3} However, successful commercialisation of OPV devices will only happen when three basic requirements are fulfilled at the same time: reasonable PCE, lifetime and cost.\textsuperscript{4} Currently the PCE of OPV devices is only about 10\%\textsuperscript{1}, which is low compared to the PCE of silicon-based PV devices.

Presently, the best performing single-junction (\emph{i.e.}, solar cell configuration consisting of one cell) OPV devices are based on the concept of the three-dimensional (bulk) heterojunction (BHJ).\textsuperscript{4} In this type of device the photo-active layer consists of bi-continuous and interpenetrating networks of phase-separated donor and acceptor domains that ideally should not be larger than the exciton diffusion length. In this way, all excitons are able to reach the donor-acceptor interface before they recombine. The hole-conducting donor typically is a conjugated polymer that absorbs most of the light. Record PCEs are obtained with OPV devices that contain donor-acceptor co-polymers as the donor material.\textsuperscript{5,6} In donor-acceptor co-polymers electron-rich donating and electron-poor accepting fragments are coupled together in one monomeric unit, which reduces the band gap and enhances light absorption towards the near infrared spectral region.\textsuperscript{7,8}

\*r.w.a.havenith@rug.nl; phone +31 50 363 7754; fax +31 50 363 4441


Proc. of SPIE Vol. 9567 95670N-1
The electron-conducting acceptor usually is a fullerene derivative. A well-known and often applied fullerene derivative is [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM).

To understand why the PCE of organic solar cells is rather low, we need to study the OPV working mechanism. The commonly accepted scheme consists of the following steps: light absorption by mainly the donor leading to the formation of tightly bound electron-hole pairs (i.e., excitons), diffusion of these excitons towards the donor-acceptor interface, electron transfer from donor to acceptor, transport of free charges to the electrodes and finally charge collection. Due to the low dielectric constant of organic semiconductors, tightly bound electron-hole pairs are formed on the polymer after light absorption.

Despite this attained understanding, the generation of free charges in OPV devices is still not fully understood. Besides intra-molecular local excitons on the polymer, many experimental studies demonstrate the presence of inter-molecular charge-transfer (CT) excitons that may be generated at the donor-acceptor interface by electron transfer. The interfacial CT state can be seen as an intermediate state between the initially excited state and the final charge-separated (CS) state. Often the lowest CT state (CT_1) of the CT manifold is lower in energy than the final CS state. The energy difference is believed to be one of the most important parameters that limit the PCE of OPV devices.

Clarke et al. define two different binding energies for the intra-molecular local excitons and the inter-molecular CT excitons to emphasise their difference. The first definition considers the binding energy of the initially formed local exciton. This property is equal to the energy difference between the CS state consisting of two fully dissociated charges in the same material and the initially formed local exciton. This binding energy will be labelled $E_b^{\text{exc}}$ from now on (Figure 1). Estimates of $E_b^{\text{exc}}$ for conjugated polymers range from less than 0.1 eV to over 1 eV. Several experimental and theoretical studies showed that different types of excitons with varying $E_b^{\text{exc}}$ are formed as the primary photo-excitations in polymers. The less bound excitons are believed to play a significant role in the photovoltaic process because they might decrease the energy and voltage loss for charge separation, reduce geminate recombination, and make electron transfer from donor to acceptor easier.

The second definition of Clarke et al. considers the binding energy of the CT exciton. The energy difference between the CS state consisting of two fully dissociated charges in the donor and acceptor molecules and the nearest neighbour CT state at the donor-acceptor interface, is called the CT exciton binding energy and labelled $E_b^{\text{CT}}$ from now on (Figure 1). This energy difference is estimated to be a few tenths of an eV. Consequently, the electron and hole are not able to escape from their Coulomb attraction in order to generate free charges. In general, if the binding energy of either the local or CT exciton is higher than the available thermal energy, which is a few hundredths of an eV, the electron and hole remain bound.

![Figure 1. Local exciton at the donor monomer 4,4′-bis-(2-methyl)-4H-cyclopenta[2,1-b;3,4-b′]-dithiophene-4-(2-thienyl)-2,1,3-benzothiadiazole (CPDTTBT) illustrating the exciton binding energy ($E_b^{\text{exc}}$) and inter-molecular CT exciton at the donor CPDTTBT and the acceptor PCBM illustrating the CT exciton binding energy ($E_b^{\text{CT}}$). (blue: positive charge, red: negative charge)
Different mechanisms exist that explain how the charge generation process in organic solar cells can overcome the high $E_b^{CT}$. One of the most popular ones assumes that excess photon energy leads to hot CT states that assist in charge separation. Bakulin et al.\textsuperscript{22} found experimental evidence in the enhancement of the photo-current due to re-excitation in the CT manifold. Still, the question whether this hot CT state assisted mechanism is common to photo-induced charge separation processes in general, remains challenging to answer. Recently, an experimental study performed by Vandewal et al.\textsuperscript{15} indicated that free charge carriers are generated and collected with nearly identical efficiencies regardless of whether the charges are generated on excitation directly into the CT\textsubscript{1} state or on excitation into higher energy, unrelaxed CT states, higher energy donor excited states and higher energy acceptor excited states. Vandewal et al.\textsuperscript{15} propose that all hot CT states relax within the CT manifold and are in thermal equilibrium with CT\textsubscript{1}, which suggests that excess energy cannot be exploited to improve the charge separation yield.\textsuperscript{17}

An electronic state diagram of the solar energy conversion to free charges is shown in Figure 2. The blue arrows show the basic steps to create free charges assisted by hot (grey lines) and higher energy electronic CT states (black line labelled CT\textsubscript{n}). The green arrows show the energy difference defined as $E_b^{CT}$ and the CS state energy, which is the energy difference between the ionisation potential (IP) of the donor and electron affinity (EA) of the acceptor.

![Electronic state diagram of the first steps of the OPV working mechanism.](image)

Figure 2. Electronic state diagram of the first steps of the OPV working mechanism. Vibrational energy levels within the CT manifold are depicted in grey. Higher energy electronic D* states are omitted for clarity. (D* = donor excited state, D\textsuperscript{*} = radical cation of donor, A\textsuperscript{*} = radical anion of acceptor)

Szarko et al.\textsuperscript{23} are of the opinion that understanding the role of charge separation via intra- and inter-molecular charge transfer mechanisms is of great importance for comprehending the OPV functional performance. They state that the role of intra-molecular CT states and their dependence on the push-pull character of the polymer has received little attention, mainly because intra-molecular charge transfer and charge separation processes were thought to be unimportant for OPV device performance. However, Szarko et al.\textsuperscript{23} showed that for PTB7:PCBM blends free charges are actually generated via a combination of intra- and inter-molecular charge transfer mechanisms.\textsuperscript{23}

Howard et al.\textsuperscript{24} showed for P3HT:PCBM blends that quenching of the local excitons on P3HT via electron transfer leads to two populations: inter-molecular CT excitons and the immediate formation of free charges. It appeared that all CT excitons recombine and therefore do not contribute to the photo-current. Therefore, in this blend free charges are generated without passing through the inter-molecular CT state as intermediate state.\textsuperscript{24}

Based on experimental results, Rolczynski et al.\textsuperscript{25} conclude that a more polar local exciton on the polymer is more likely to produce a better separated electron and hole and therefore to produce free charges in BHJ devices. Their study focuses on the role of the local exciton polarity on the exciton dissociation dynamics at the donor-acceptor interface. They showed that a higher exciton polarity enhances charge dissociation within tens to hundreds of picoseconds after the excitation. The local dipole moment change upon excitation of a single repeating unit of the polymer ($\Delta \mu_{loc}$) is used to characterise the local exciton polarity. A higher exciton polarity can be obtained by push-pull actions between the neighbouring building blocks of the co-polymer. It is proposed that a correlation exists between the local charge transfer character in the co-polymer and the corresponding BHJ device performance through the intrinsic polarity of the exciton.\textsuperscript{25}
These studies all make clear that charge separation in OPV devices via intra- and/or inter-molecular charge transfer mechanisms is still not fully understood. Szarko et al.\textsuperscript{23} expect that a (possible) interplay between intra- and inter-molecular CT states has significant implications for how to optimise the BHJ morphology to obtain better performing OPV devices. Regarding such a possible interplay, an unanswered question is whether a relation exists between the binding energy of the local exciton (\textit{i.e.,} intra-molecular CT state) and the binding energy of the CT exciton (\textit{i.e.,} inter-molecular CT state). Lowering the binding energies of both types of excitons is expected to contribute to better performing OPV devices since charges can be separated via intra- and/or inter-molecular charge transfer mechanisms as Howard \textit{et al.}\textsuperscript{24} and Szarko \textit{et al.}\textsuperscript{23} showed.

The objective of this work is three-fold. According to Rolczynski \textit{et al.}\textsuperscript{25} \(\Delta \mu_{ge}\) (defined for a monomer unit) reflects the local electron density displacement upon excitation and can be used to characterise the local exciton polarity, which in turn gives information about the possibility to create free charges. This suggests that changes in the local exciton polarity are related to changes in the amount of charge that is transferred upon excitation and/or changes in the separation between the positive and negative charge formed upon excitation of a monomer. These characteristics of the excitation process provide detailed and complementary information on the charge separation process upon excitation. Therefore, in the first place, we study these characteristics and their (possible) relation to \(E_b^{\text{exc}}\) for a series of related donor-acceptor co-monomers and their corresponding trimers (Figure 3). From the electron density difference between the excited and ground state, \(\Delta \rho(r)\), the amount of transferred charge between segments upon excitation using a Mulliken population analysis\textsuperscript{26} is obtained. Different methods have been proposed to quantify the charge transfer character of an electronic transition and the charge transfer excitation length. Etienne \textit{et al.}\textsuperscript{27, 28} suggest the use of detachment and attachment densities, which physically depict the hole and electron generated upon excitation. Here, the spatial distance between the two barycentres of the regions where an electron density loss or gain is generated upon excitation, is calculated following the procedure put forward by Le Bahers \textit{et al.}\textsuperscript{29}. This distance is a measure of the charge transfer excitation length, labelled \(D_{CT}\). The charge separation upon excitation is visualised by computing an isosurface of \(\Delta \rho(r)\).

Secondly, since in real OPV devices polymers are embedded in a blend and not isolated, we investigate the effect of an embedding on the vertical local exciton binding energy (\(E_b^{\text{exc}}\)) of the same series of monomers using the polarisable continuum model (PCM)\textsuperscript{30}. In this way we can answer the question whether these embedding effects influence the trend that was found in vacuum for \((E_b^{\text{exc}})_{\text{vert}}\)\textsuperscript{31}.

Thirdly, we study whether a relation exists between the binding energies of local and CT excitons for the same series of monomers. Isolated monomer-PCBM complexes are used to calculate the properties of the CT excitons.

![Figure 3. Chemical structures of monomers (n = 1) 1-6 and their corresponding trimers (n = 3) T1-T6. Monomer 1 is the reference monomer CPDTTBT. Isomers 2 and 3 are linear-conjugated and 4 and 5 are cross-conjugated. Monomers 2-5 contain mesomeric push-pull groups and monomer 6 contains inductive push-pull groups.](image)

We concentrated on a series of related donor-acceptor co-monomers (Figure 3) that have different \((E_b^{\text{exc}})_{\text{vert}}\), resulting from the different push-pull group substitution patterns, and different local exciton polarities, shown by different \(\Delta \mu_{ge}\). In this series, the reference monomer 1 is CPDTTBT, a well-known donor-acceptor co-monomer, which consists of the donating fragment CPDT and the accepting fragment BT, linked via one thiophene unit T. Such a thiophene unit is often included in the donor-acceptor co-polymer design to make the backbone more planar.\textsuperscript{6}
2. COMPUTATIONAL DETAILS

2.1 Charge transfer and charge separation upon excitation

Geometries of the isolated monomers 1-6 were optimised using Density Functional Theory (DFT) (BHandH\textsuperscript{32}/6-31G**) with the program DALTON\textsuperscript{33} and geometries of the isolated trimers T1-T6 with the program GAMESS-UK\textsuperscript{34}. The arguments for choosing BHandH to describe these systems can be found elsewhere\textsuperscript{31,35}. The lowest vertical excitation energy and corresponding excited state density \( \rho_{\text{exc}}(t) \) were calculated with time-dependent DFT (TD-DFT) (BHandH/6-31G**) using the program GAUSSIAN09\textsuperscript{36}. For all monomers and trimers, the primary photo-excitation (i.e., the excitation with the largest oscillator strength) is the first excited state. For all systems except T4 the largest contribution for this state comes from a HOMO \( \rightarrow \) LUMO one-electron transition on the monomer/trimer. For T4, the HOMO \( \rightarrow \) LUMO (\( c^2 = 0.25 \)) and HOMO-1 \( \rightarrow \) LUMO transitions (\( c^2 = 0.26 \)) are equally important.\textsuperscript{31} Ground \( (\rho_{\text{g}}(t)) \) and excited state densities were calculated on a grid of points using the cubegen program of GAUSSIAN 09. For the first excited state, the electron density displacement upon excitation, \( \Delta \rho(r) \), was calculated by taking the difference between \( \rho_{\text{g}}(t) \) and \( \rho_{\text{exc}}(t) \). Plots of an isosurface of \( \Delta \rho(r) \) were generated with GAUSSVIEW to visualise the charge transfer upon excitation of the monomer/trimer.

Subsequently, \( \Delta \rho(r) \) was used to calculate \( D_{\text{CT}} \) according to the procedure outlined by Le Bahers et al.\textsuperscript{29}. The barycentres of the spatial regions where an electron density loss or gain is generated upon excitation, respectively \( \rho_+(r) \) and \( \rho_-(r) \), were calculated in the following way:

\[
R_+ = \frac{\int \rho_+(r) dr}{\int \rho_+(r) dr} = (x_+, y_+, z_+) \tag{1}
\]

and analogously for \( \rho_-(r) \) leading to \( R_- \). By integrating \( \rho_+(r) \) or \( \rho_-(r) \) over all space the total amount of transferred charge, \( q_{\text{CT}} \), was obtained. The spatial distance between the two barycentres, \( D_{\text{CT}} \), was given by:

\[
D_{\text{CT}} = |R_+ - R_-| \tag{2}
\]

As Le Bahers et al.\textsuperscript{29} pointed out, the result of multiplying \( D_{\text{CT}} \) with \( q_{\text{CT}} \) has to be equal to the value of \( \Delta \mu_{\text{gs}} \).

The difference between the Mulliken charges of the first excited and ground state, grouped per segment, was used to quantify the amount of transferred charge between the segments during the excitation (GAUSSIAN09). It appears that in monomer 1 and 4-6 very little charge (\( \sim 0.04 \, |e| \)) is transferred in the ground state. Monomers 2 (0.13 \( |e| \)) and 3 (0.12 \( |e| \)) show a slightly larger transfer in the ground state. In all trimers a reasonably small amount of charge is transferred in the ground state (range: 0.1-0.4 |e|). A comparison between the Mulliken charge differences and charge differences obtained by a natural population analysis\textsuperscript{37} (NPA with GAUSSIAN09) for monomers 1 and 5 grouped per segment showed that similar results for both methods were found (see Figure 4 for the results of the Mulliken analysis). Based on this similarity we conclude that the numbers obtained by a summation of atomic charge population differences for a specific part of the molecule are not very dependent on the choice of charge analysis. Therefore, in this study the Mulliken population analysis is used for this purpose.

To check the validity of the (TD-)DFT results for the vertical first excited state energy and the amount of charge transfer upon excitation, state specific (SP) and state average (SA) CASSCF(16,12) calculations with a 6-31G** and ANO-S basis set of TZP quality (S 5s 4p 1d /C/N/O 4s 3p 1d /H 3s 1p) were performed for monomer 1 using the program MOLCAS\textsuperscript{38,40}. Only the SP and SA CASSCF (ANO-S) calculations were followed by CASPT2 calculations because this method requires a sufficiently large basis set. The active space consisted of the 8 highest occupied and 4 lowest unoccupied \( \pi \)-orbitals.
2.2 Effect of an embedding on the vertical local exciton binding energy

Single-point neutral, cationic and anionic polarisable continuum model DFT (PCM-DFT) (restricted open-shell DFT in the case of the cationic and anionic calculations) and single-point first excited state PCM-TDDFT (BHandH/6-31G**) calculations with increasing static dielectric constant \( \varepsilon_r \) (range: 1-15) were performed with the program DALTON, all at the optimised ground state geometry of the monomers 1-6. At every \( \varepsilon_r \), \((E_b^{\text{exc}})_{\text{vert}}\) of the monomers 1-6 was given by the energy difference between the vertical CS state of the monomer - calculated as the energy difference between the vertical IP \((\text{IP})_{\text{vert}}\) and vertical EA \((\text{EA})_{\text{vert}}\) - and the vertical first excited state of the monomer.

2.3 Monomer-PCBM complexes

Geometries of monomers 1-6 with PCBM in their vicinity were optimised using dispersion-corrected DFT (DFT-D3) (BHandH/6-31G**) with the program GAMESS-UK. In a previous study\(^{35}\) DFT-D (B3LYP\(^{32}/6\text{-}31G**\)) geometry optimisations on four initial configurations of a monomer-PCBM complex were performed (GAMESS-UK) to determine a representative configuration. Here, the lowest energy configuration was used as a starting point for the geometry optimisation of these monomer-PCBM complexes. Neutral, cationic and anionic geometry optimisations were performed (unrestricted DFT in the case of the cationic and anionic complexes).

The lowest 10 vertical excitation energies, and in the case of monomer 1-PCBM and monomer 6-PCBM the lowest 20, were calculated on the neutral optimised geometries using TD-DFT (BHandH/6-31G**) with DALTON. TD-DFT was used to obtain the excited state with the largest CT character from monomer to PCBM (labelled \((\text{CT})_{\text{vert}}\)). Whether the excitation has CT character was estimated from the weight of the HOMO → LUMO one-electron transition to a given excitation: the HOMO is located at the donor molecule (monomer) and the LUMO at the acceptor molecule (PCBM). \((\text{CT})_{\text{vert}}\) is \(S_2\) for monomer 1-PCBM, \(S_1\) for monomer 2-PCBM, \(S_1\) for monomer 3-PCBM, \(S_1\) for monomer 4-PCBM, \(S_1\) for monomer 5-PCBM, and \(S_1\) for monomer 6-PCBM. For monomer 1-PCBM and monomer 4-PCBM, all excited states below \(S_1\) are local PCBM-excitations, which are nearly degenerate with the CT excitation.

The vertical CT exciton binding energy \((E_b^{\text{CT}})_{\text{vert}}\) is defined as the energy difference between the vertical CS state of the monomer-PCBM complex and the vertical CT state of the complex:

\[
(E_b^{\text{CT}})_{\text{vert}} = (\text{IP})_{\text{vert}} - (\text{EA})_{\text{vert}} - (\text{CT})_{\text{vert}}
\]  

(3)

with \((\text{IP})_{\text{vert}}\) the vertical ionisation potential, \((\text{EA})_{\text{vert}}\) the vertical electron affinity, and \((\text{CT})_{\text{vert}}\) the vertical CT state energy of the complex (\text{i.e., vertical implies that all energies are obtained at the optimised ground state geometry of the complex}).

The relaxed CT exciton binding energy \((E_b^{\text{CT}})_{\text{relaxed}}\) is defined as the energy difference between the relaxed CS state of the complex and the vertical CT state of the complex:

\[
(E_b^{\text{CT}})_{\text{relaxed}} = IP - EA - (\text{CT})_{\text{vert}}
\]  

(4)

with IP the relaxed ionisation potential, EA the relaxed electron affinity, and \((\text{CT})_{\text{vert}}\) the vertical CT state energy of the complex. The effect of geometry relaxation of the CS state on the lowering of \(E_b^{\text{CT}}\) is included since the lifetime of the CS state is considerably longer (\text{i.e., several ns}) than the typical timescales of molecular vibrations (\text{i.e., on the order of ps}). The creation of free charges from the CT state typically takes place within 150 fs\(^{43}\), which is shorter than the typical timescales of molecular vibrations. Therefore the effect of geometry relaxation of the CT state on \(E_b^{\text{CT}}\) is not included in this study.

Since the calculations were done on isolated monomer-PCBM complexes, the theoretical values for \(E_b^{\text{CT}}\) are higher compared to experimental values because stabilisation effects from the environment and charge delocalisation effects are missing.
3. RESULTS AND DISCUSSION

3.1 Charge transfer and charge separation upon excitation

3.1.1 Monomers

Plots of the isosurface of $\Delta \rho(r)$ for monomers 1-6 are shown in Figure 4. Below each plot the difference between the Mulliken charges of the first excited and ground state is given, grouped per segment. The values of $D_{CT}$ and $q_{CT}$ are included in each plot too.

For all monomers the plots of an isosurface of $\Delta \rho(r)$ show that charge is transferred during the excitation from the donating segment and the thiophene unit (predominantly blue, i.e., loss of electron density) to the accepting segment (predominantly red, i.e., gain in electron density). So the thiophene unit actively participates in the charge transfer process. Large and distinct differences between the monomers in the charge separation upon excitation are not immediately visible from these plots. Upon these $\pi \rightarrow \pi^*$ transitions, not only electron transfer in the $\pi$-system is visible, but also changes in the $\sigma$ electron density are discernible, due to relaxation.
The Mulliken charge differences between the first excited and the ground state, grouped per segment, (Figure 4, below each plot) show that for monomers 2-5 ~0.4 [\epsilon^e] is transferred during the excitation from the donating segment and the thiophene unit to the accepting segment. At monomer 1 only 0.27 [\epsilon^e] is transferred between these segments, so substitution with mesomeric push-pull groups enhances the amount of transferred charge upon excitation. In the case of inductive push-pull groups (monomer 6) the amount of transferred charge between these segments (0.32 [\epsilon^e]) is slightly smaller compared to 2-5, because these groups do not act through the π-bond system, while this excitation has mainly \pi→\pi^* character. Still these groups enhance the amount of charge transfer too, compared to 1.

Our results show that the thiophene unit actively participates in the charge transfer process by enhancing the amount of charge transfer. Choosing a particular substitution pattern can influence this enhancement. For example in monomer 3 the thiophene unit is a stronger donor than the donating segment itself. Banerji et al.\textsuperscript{44} reported for a particular donor-accepter co-polymer (PCDTBT) that the thiophene moiety itself relative to the accepting segment is electron donating. For PCDTBT, the electron donating properties of the bridging thiophene are stronger than of the actual donating segment. PCDTBT is related to our monomer of interest, since it only differs in choice of the donating segment (CB instead of CPDT). Our result for monomer 3 is in line with this finding of Banerji et al.\textsuperscript{44}.

The values of \Delta_{DCT} (Figure 4, included in each plot) differ between the monomers. Monomers 2-3 show slightly smaller and 4-5 slightly larger values compared to 1 and 6, which show similar values. This trend gives insight in the trend found in \Delta_{\mu_{\text{ge}}} (Table S1 in the Supporting Information), because \textbf{q}_{CT} differs only moderately between the monomers. So it may be useful to separate \Delta_{\mu_{\text{ge}}} in its individual components \Delta_{DCT} and \textbf{q}_{CT} to obtain detailed information about the excitation process. For example, the larger \Delta_{\mu_{\text{ge}}} of 4-5 compared to 2-3 originates from their larger \Delta_{DCT} and slightly larger \textbf{q}_{CT}. For 6, its larger \Delta_{\mu_{\text{ge}}} compared to 2-3 originates from its larger \Delta_{DCT}, because its \textbf{q}_{CT} is nearly similar with the \textbf{q}_{CT} of 2-3. Compared to 4-5, 6 has a smaller \Delta_{\mu_{\text{ge}}}, which originates from its smaller \Delta_{DCT} and slightly smaller \textbf{q}_{CT}. Due to its small \Delta_{DCT} and smallest \textbf{q}_{CT}, 1 has a small \Delta_{\mu_{\text{ge}}}. The smallest \Delta_{\mu_{\text{ge}}} was found for 3, which can be explained with its smallest \Delta_{DCT}.

If all these characteristics of the excitation process are compared with the trend found in \(E_{\text{B}}^{\text{exc}}\text{vert}\) (Table S1), it appears that many of the differences herein between the monomers can be understood. For example, the highest \(E_{\text{B}}^{\text{exc}}\text{vert}\) for monomer 3 can be explained with its smallest \Delta_{DCT}, the small \(E_{\text{B}}^{\text{exc}}\text{vert}\) for 4 and 5 with their large \Delta_{DCT} and \textbf{q}_{CT}, and the similar \(E_{\text{B}}^{\text{exc}}\text{vert}\) for 1 and 6 with their similar \textbf{q}_{CT} and \Delta_{DCT}.

To check the performance of this (TD-)DFT approach, CASSCF followed by CASPT2 calculations were done for monomer 1 (Table S2 in the Supporting Information). It appears that the vertical first excited state energy calculated with TD-DFT (BHandH/6-31G**) and CASPT2 (ANO-S) agrees within ~0.2 eV. Quantitative differences appear in the Mulliken charge differences (Exc-Gr) between the different quantum chemical methods, with more charge transfer from the thiophene to the acceptor unit for the CASSCF calculation, suggesting that the (TD-)DFT approach underestimates the charge transfer character of these excitations; however, the Mulliken charge differences obtained with (TD-)DFT are in qualitative agreement with those from the CASSCF calculations.

This study makes clear that a plot of the isosurface of \(\Delta p(r)\), the amount of charge transfer upon excitation, and the charge transfer excitation length provide detailed and complementary information about the excitation process. For this series of monomers, such a detailed study of the excitation process reveals that the thiophene unit actively participates in the charge transfer process and that its contribution can be tuned by choosing a particular push-pull group substitution pattern.

### 3.1.2 Trimers

In order to see if the findings for the monomers still hold when larger systems are studied, we investigated the same characteristics of the excitation process for trimers T1-T6. Plots of the isosurface of \(\Delta p(r)\), together with the Mulliken charge difference between the first excited and the ground state, grouped per segment, are given in Figure 5. The values of \(D_{\text{CT}}\) and \textbf{q}_{CT} are included in each plot too. Large and distinct differences between the trimers in the charge separation upon excitation are not immediately discernible. Just like in the monomeric systems, charge is transferred from the donating segments and the bridging thiophene units - which actively participate in the charge transfer process - to the accepting segments. For all trimers, the excitations are more or less delocalised over the whole molecule.
The Mulliken charge differences between the first excited and the ground state, grouped per segment, (Figure 5, below each plot) make clear that the total amount of transferred charge during the excitation from the donating segments and the thiophene units to the accepting segments is reasonably similar for \( T2 \) (0.28 \(|e^-|\)), \( T3 \) (0.30 \(|e^-|\)), \( T4 \) (0.25 \(|e^-|\)), \( T5 \) (0.28 \(|e^-|\)) and \( T6 \) (0.23 \(|e^-|\)) and slightly smaller for the reference \( T1 \) (0.19 \(|e^-|\)). Also for the trimeric systems it appears that the thiophene units participate in the charge transfer process and that the push-pull groups enhance the amount of charge transfer upon excitation.

The values of \( D_{CT} \) (Figure 5, included in each plot) vary in a narrow range for the trimers. For all trimers the values of \( D_{CT} \) are smaller than the ones found for the monomeric systems (Figure 4) because of the more delocalised nature of the excitations leading to averaging of the positive/negative charge positions over all three units and, hence, a small \( D_{CT} \). Just like for the monomers, also for the trimers the trend in \( D_{CT} \) gives insight in the trend found in \( \Delta \mu_{ge} \) (Table S1), because \( q_{CT} \) is reasonably similar for \( T2\)-\( T6 \). For example, the large \( \Delta \mu_{ge} \) for \( T3 \) originates from its large \( D_{CT} \) and the small \( \Delta \mu_{ge} \) for \( T6 \) from its small \( D_{CT} \). The smaller \( \Delta \mu_{ge} \) of \( T4 \) compared to \( T2\)-\( T3 \) and \( T5 \) can be explained with its smaller \( D_{CT} \) and its slightly smaller \( q_{CT} \). Finally, \( T1 \) shows a smaller \( D_{CT} \) and \( q_{CT} \) compared to \( T2\)-\( T6 \) and therefore its \( \Delta \mu_{ge} \) is the smallest. So also the trimers show that it may be useful to separate \( \Delta \mu_{ge} \) in its individual components \( D_{CT} \) and \( q_{CT} \) to obtain detailed information about the excitation process.

\[
\begin{align*}
D_{CT} &= 0.75 \, \text{Å} \\
q_{CT} &= 0.59 \, |e^-| \\
\text{T1}
\end{align*}
\]

\[
\begin{align*}
D_{CT} &= 1.13 \, \text{Å} \\
q_{CT} &= 0.70 \, |e^-| \\
\text{T2}
\end{align*}
\]

\[
\begin{align*}
D_{CT} &= 1.25 \, \text{Å} \\
q_{CT} &= 0.69 \, |e^-| \\
\text{T3}
\end{align*}
\]
Isosurface (isocontour value: 0.0001 a.u.) of $\Delta \rho(r)$ for trimers T1-T6 with below each plot the difference between the Mulliken charges of the first excited and ground state, grouped per segment, and in the upper left corner of each plot the value of $D_{CT}$ and $q_{CT}$. Blue corresponds to a loss of electron density, red corresponds to a gain in electron density. Length of each trimer: ~50 Å.

If all these characteristics of the excitation process are compared with the trend found in $(E_b^\text{exc})_{\text{vert}}$ of the trimers (Table S1), there appears to be no relation between $(E_b^\text{exc})_{\text{vert}}$ and one of the aforementioned characteristics ($D_{CT}$, $q_{CT}$, $\Delta \mu_{ge}$) that for example can explain the slightly lower $(E_b^\text{exc})_{\text{vert}}$ in the case of T5.

3.2 Effect of an embedding on the vertical local exciton binding energy

The effect of a uniform polarisable environment on $(E_b^\text{exc})_{\text{vert}}$ of monomers 1-6 is shown in Table 1 and Figure 6. Upon increasing $\varepsilon_r$, a reasonably similar decrease in $(E_b^\text{exc})_{\text{vert}}$ for monomers 1-6 is observed, which does not influence the trend found in $(E_b^\text{exc})_{\text{vert}}$ for the isolated monomers\(^\text{31}\). This result can be rationalised because the electron density displacement upon excitation and the Mulliken charge difference between the excited and ground state (Figure 4) are also reasonably similar for the monomers 1-6, leading to a comparable interaction with the environment. So it appears that the observed differences in the amount of charge transfer and charge separation upon excitation between the monomers, which were discussed previously (see paragraph 3.1), do not influence the stabilisation effects and therefore the trend found in $(E_b^\text{exc})_{\text{vert}}$ for the isolated monomers is not affected.
Table 1. Vertical local exciton binding energies (eV) as a function of the static dielectric constant for monomers 1-6.

<table>
<thead>
<tr>
<th>$\varepsilon_r$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.70</td>
<td>2.61</td>
<td>2.79</td>
<td>2.46</td>
<td>2.42</td>
<td>2.73</td>
</tr>
<tr>
<td>3</td>
<td>0.84</td>
<td>0.76</td>
<td>0.93</td>
<td>0.55</td>
<td>0.50</td>
<td>0.76</td>
</tr>
<tr>
<td>6</td>
<td>0.35</td>
<td>0.29</td>
<td>0.44</td>
<td>0.04</td>
<td>0.00</td>
<td>0.22</td>
</tr>
<tr>
<td>9</td>
<td>0.18</td>
<td>0.13</td>
<td>0.28</td>
<td>-0.13</td>
<td>-0.17</td>
<td>0.10</td>
</tr>
<tr>
<td>12</td>
<td>0.10</td>
<td>0.04</td>
<td>0.21</td>
<td>-0.22</td>
<td>-0.25</td>
<td>0.02</td>
</tr>
<tr>
<td>15</td>
<td>0.05</td>
<td>-0.01</td>
<td>0.13</td>
<td>-0.27</td>
<td>-0.31</td>
<td>-0.03</td>
</tr>
</tbody>
</table>

$\Delta (E_{b}^{exc})_{vert}$ (eV)

|               | 2.66 | 2.62 | 2.66 | 2.72 | 2.72 | 2.76 |

In a typical OPV device the relative dielectric constant of the active layer (polymer and PCBM) is ~3-4. Figure 6 shows that a dielectric screening of 3 lowers $(E_{b}^{exc})_{vert}$ by ~2 eV. For the cross-conjugated monomers 4 and 5 $(E_{b}^{exc})_{vert}$ is lowered to ~0.5 eV, which is in good agreement with reported values for similar donor-acceptor co-polymers (i.e., 0.3-0.5 eV).

3.3 Monomer-PCBM complexes

3.3.1 Excited state properties

An overview of several excited state properties for monomers 1-6 with PCBM is given in Table 2. It appears that $\varepsilon_{LUMO}$ becomes similar for all monomer-PCBM complexes within a range of 0.1 eV because this property is predominantly determined by $\varepsilon_{LUMO}$ of the PCBM molecule. For $\varepsilon_{HOMO}$ the same trend is found in the monomer-PCBM complexes as was found in the corresponding monomer systems (Table S3 in the Supporting Information). These outcomes are in line with the general picture that for a donor-acceptor complex $\varepsilon_{HOMO}$ resembles $\varepsilon_{HOMO}$ of the donor and $\varepsilon_{LUMO}$ resembles $\varepsilon_{LUMO}$ of the acceptor. The band gap $\Delta\varepsilon_{H}$ becomes nearly similar for all complexes due to the similar $\varepsilon_{LUMO}$ and almost similar $\varepsilon_{HOMO}$. A reasonable correspondence in the trends between $(IP)_{vert}$ and $\varepsilon_{HOMO}$ and a good correspondence in trends between $(EA)_{vert}$ and $\varepsilon_{LUMO}$ for the complexes is found.

A slightly larger relaxation energy of the cation (i.e., $(IP)_{vert} - IP$) is found in the case of monomer 5-PCBM, namely ~0.3 eV, compared to the other complexes, namely ~0.2 eV. A noteworthy change in geometrical feature upon relaxation...
of the cationic complexes is the decrease in dihedral angle \( \alpha \), resulting in planarisation of the monomer (Figure 7). The relaxation energies of the anions (i.e., \((EA)_\text{vert} - EA\)) are similar for all complexes, namely \( \sim 0.1 \) eV, because the PCBM molecule predominantly determines the relaxation of the anionic complex.

![Geometry of neutral complex and cationic complex](image)

Figure 7. Left: geometry of neutral complex of monomer 5-PCBM illustrating the relative large dihedral angle \( \alpha \). Right: geometry of cationic complex of monomer 5-PCBM illustrating the smaller dihedral angle \( \alpha \).

\((CT)_{\text{vert}}\) is expected to depend on \((IP)_{\text{vert}}\) of the monomer-PCBM complex (which is related to \((IP)_{\text{vert}}\) of the monomer, Table S3), \((EA)_{\text{vert}}\) of the complex (which is related to \((EA)_{\text{vert}}\) of PCBM) and the distance between the monomer and PCBM. Table 2 shows comparable \((EA)_{\text{vert}}\) for the complexes. Also the nearest distance between the monomer and PCBM carbon atoms (the ones of the \( C_60 \) part) is comparable for the complexes (3.02 \( \pm 0.1 \) \( \AA \)). So the trend in \((CT)_{\text{vert}}\) is expected to depend on the trend in \((IP)_{\text{vert}}\) of the complexes. Indeed a reasonable linear correlation \((R^2 = 0.63)\) is found between \((IP)_{\text{vert}}\) and \((CT)_{\text{vert}}\), i.e., the smaller the \((IP)_{\text{vert}}\) the lower \((CT)_{\text{vert}}\). The strongest linear correlation is found between \((IP)_{\text{vert}}\) - \((EA)_{\text{vert}}\) and \((CT)_{\text{vert}}\) \((R^2 = 0.80)\).

Table 2. The vertical excitation energy of the excited state with the largest oscillator strength \(((S^*)_{\text{vert}}, eV)\), vertical CT state energy \(((CT)_{\text{vert}}, eV)\), oscillator strength of the vertical excited state with the largest oscillator strength \(f_{(S^*)}\), oscillator strength of the vertical CT state \(f_{(CT)}\), HOMO energy \(\epsilon_{\text{HOMO}}, eV\), LUMO energy \(\epsilon_{\text{LUMO}}, eV\), orbital energy difference between HOMO and LUMO \((\Delta \epsilon_{\text{HL}}, eV)\), vertical ionisation potential \((IP)_{\text{vert}}, eV\), ionisation potential \((IP, eV)\), vertical electron affinity \((EA)_{\text{vert}, eV}\), and electron affinity \((EA, eV)\) for monomers 1-6 with PCBM.

<table>
<thead>
<tr>
<th>system</th>
<th>((S^*)_{\text{vert}})</th>
<th>((CT)_{\text{vert}})</th>
<th>(f_{(S^*)})</th>
<th>(f_{(CT)})</th>
<th>(\epsilon_{\text{HOMO}})</th>
<th>(\epsilon_{\text{LUMO}})</th>
<th>(\Delta \epsilon_{\text{HL}})</th>
<th>((IP)_{\text{vert}})</th>
<th>IP</th>
<th>((EA)_{\text{vert}})</th>
<th>EA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-PCBM</td>
<td>2.93</td>
<td>2.47</td>
<td>0.12</td>
<td>0.0050</td>
<td>-5.77</td>
<td>-2.23</td>
<td>3.54</td>
<td>6.13</td>
<td>5.91</td>
<td>1.68</td>
<td>1.78</td>
</tr>
<tr>
<td>2-PCBM</td>
<td>2.20</td>
<td>0.053</td>
<td>0.53</td>
<td>0.0050</td>
<td>-5.76</td>
<td>-2.33</td>
<td>3.43</td>
<td>6.04</td>
<td>5.85</td>
<td>1.83</td>
<td>1.97</td>
</tr>
<tr>
<td>3-PCBM</td>
<td>2.34</td>
<td>0.21</td>
<td>0.21</td>
<td>0.0050</td>
<td>-5.81</td>
<td>-2.21</td>
<td>3.60</td>
<td>6.10</td>
<td>5.90</td>
<td>1.69</td>
<td>1.80</td>
</tr>
<tr>
<td>4-PCBM</td>
<td>2.56</td>
<td>0.12</td>
<td>0.027</td>
<td>0.0050</td>
<td>-5.83</td>
<td>-2.28</td>
<td>3.55</td>
<td>6.19</td>
<td>5.98</td>
<td>1.78</td>
<td>1.94</td>
</tr>
<tr>
<td>5-PCBM</td>
<td>2.39</td>
<td>0.17</td>
<td>0.051</td>
<td>0.0050</td>
<td>-5.64</td>
<td>-2.29</td>
<td>3.35</td>
<td>5.99</td>
<td>5.66</td>
<td>1.77</td>
<td>1.92</td>
</tr>
<tr>
<td>6-PCBM</td>
<td>2.88</td>
<td>0.22</td>
<td>0.03</td>
<td>0.0050</td>
<td>-5.72</td>
<td>-2.25</td>
<td>3.47</td>
<td>6.05</td>
<td>5.79</td>
<td>1.71</td>
<td>1.81</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) \(CT\) corresponds to the excited state with the largest CT character from monomer to PCBM. These excitations all correspond predominantly to a HOMO (D) \(\rightarrow\) LUMO (A) transition with \(c^2 > 0.55\), except for monomer 1-PCBM (HOMO (D) \(\rightarrow\) LUMO (A) transition with \(c^2 = 0.34\) and HOMO-1 (A) \(\rightarrow\) LUMO (A) transition with \(c^2 = 0.31\) and the remaining part local PCBM-excitations), monomer 3-PCBM (HOMO (D) \(\rightarrow\) LUMO (A) transition with \(c^2 = 0.37\) and HOMO (D) \(\rightarrow\) LUMO+3 (D) with \(c^2 = 0.30\) and the remaining part local PCBM-excitations \((c^2 \sim 0.17)\) and CT excitations \((c^2 \sim 0.16)\) and monomer 4-PCBM (HOMO (D) \(\rightarrow\) LUMO (A) transition with \(c^2 = 0.38\) and HOMO-1 (A) \(\rightarrow\) LUMO (A) with \(c^2 = 0.28\) and the remaining part local PCBM-excitations).

The oscillator strengths \(f_{(CT)}\) are very small for the CT states of the complexes except for monomer 3-PCBM, which can be understood by scrutinising the occupied-virtual orbital pairs that belong to the particular CT excitation. Monomer 3-PCBM is the only system with a large D \(\rightarrow\) D contribution \((c^2 = 0.30)\) to the CT excitation, which is comparable to the D \(\rightarrow\) A contribution \((c^2 = 0.37)\). Local excitations on the donor molecule can have large oscillator strengths, which explain the large oscillator strength of the CT state of monomer 3-PCBM. It even appears to be the largest oscillator strength...
within the lowest 10 excitations. For monomer 2-PCBM the CT excitation also has, besides the dominant D → A contribution ($c^2 = 0.56$), a considerable D → D contribution ($c^2 = 0.29$), but in this system it is still significantly smaller than the most important contribution. For this complex $f_{CT}$ also is the largest oscillator strength within the lowest 10 excitations.

Table 2 also lists the vertical excitation energy of the excited state with the largest oscillator strength, labelled as $(S^*)_{vert}$ and its oscillator strength, labelled as $f_{S^*vert}$. For all monomer-PCBM complexes except monomer 2-PCBM and monomer 3-PCBM, this state is assigned predominantly as a local excitation on the monomer. For these complexes, the energies of $(S^*)_{vert}$ are comparable to the energies of the excited states with the largest oscillator strength of the monomeric systems (Table S3). For monomer 2-PCBM the second excited state at 2.37 eV with $f = 0.0052$ can be assigned as a local excitation on the monomer (D → D contribution ($c^2 = 0.46$), D → A contribution ($c^2 = 0.37$) and the remaining part local PCBM-excitations). For monomer 3-PCBM, no other excitation is found (within the lowest 10) that can be assigned predominantly as a local excitation on the monomer. Besides the CT excitation (S$_i$), also the second excited state at 2.43 eV with $f = 0.063$ has some D → D contribution ($c^2 = 0.10$), but its main character is a local-PCBM excitation ($c^2 = 0.72$).

### 3.3.2 CT exciton binding energies

For monomers 1-6 with PCBM ($E_{bCT}^{vert}$ and ($E_{bCT}^{relaxed}$ are given in Table 3. When ($E_{bCT}^{vert}$ of these monomer-PCBM complexes are compared to ($E_{bexc}^{vert}$ of the monomers 1-6 (Table S1) it appears that the clear distinction between linear- and cross-conjugation - with the lowest ($E_{bexc}^{vert}$ in the case of cross-conjugation - is not maintained in the case of ($E_{bCT}^{vert}$). In fact, all ($E_{bCT}^{vert}$ of the complexes are similar. ($E_{bCT}^{relaxed}$ appears to be slightly lower for monomer 5-PCBM (namely ~0.2 eV) compared to the other complexes. The additional reduction in this case originates from the slightly larger relaxation of the cationic complex of monomer 5-PCBM compared to the other complexes, which was mentioned previously.

The similar values of ($E_{bCT}^{vert}$ for the complexes can be explained by realising that for the monomers 1-6 the differences in ($E_{bexc}^{vert}$ between linear- and cross-conjugated molecules mainly originate from differences in (EA)$_{vert}$ (Table S3). Once a very strong acceptor (i.e., stronger than the acceptor segment of the co-monomer) like PCBM is present in the vicinity of the monomer, (EA)$_{vert}$ of the monomer itself will not affect in a direct way ($E_{bCT}^{vert}$ of the monomer-PCBM complex (eq. 3).

It turns out that (IP)$_{vert}$ of the monomer slightly affects ($E_{bCT}^{vert}$ (namely through (IP)$_{vert}$ and (CT)$_{vert}$ of the complex, see eq. 3). It appears that the variation in (IP)$_{vert}$ of the monomers (namely ~0.2 eV, Table S3) is larger than the variation in ($E_{bCT}^{vert}$ of the complexes (namely ~0.1 eV, Table 3). This indicates that the effect of (IP)$_{vert}$ of the monomer on ($E_{bCT}^{vert}$ of the complex is slightly damped.

Table 3. The vertical and relaxed CT exciton binding energy ($E_{bCT}^{vert}$, $E_{bCT}^{relaxed}$ eV) for monomers 1-6 with PCBM.

<table>
<thead>
<tr>
<th>system</th>
<th>($E_{bCT}^{vert}$)</th>
<th>($E_{bCT}^{relaxed}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-PCBM</td>
<td>1.97</td>
<td>1.65</td>
</tr>
<tr>
<td>2-PCBM</td>
<td>2.01</td>
<td>1.69</td>
</tr>
<tr>
<td>3-PCBM</td>
<td>2.07</td>
<td>1.76</td>
</tr>
<tr>
<td>4-PCBM</td>
<td>1.95</td>
<td>1.58</td>
</tr>
<tr>
<td>5-PCBM</td>
<td>1.93</td>
<td>1.46</td>
</tr>
<tr>
<td>6-PCBM</td>
<td>1.97</td>
<td>1.61</td>
</tr>
</tbody>
</table>

So for this series of monomers 1-6 no relation exists between the vertical binding energy of the local exciton and of the CT exciton because the variation in ($E_{bexc}^{vert}$ depends mainly on the large variation in (EA)$_{vert}$ between the monomers. For a series of monomers in which the variation in ($E_{bexc}^{vert}$ depends mainly on the variation in (IP)$_{vert}$ between the monomers, it is possible that ($E_{bexc}^{vert}$ and ($E_{bCT}^{vert}$ are related. However, based on our finding that the effect of (IP)$_{vert}$ on ($E_{bCT}^{vert}$ is slightly damped, a small effect is expected.
4. CONCLUSIONS

The scientific objective of this work was three-fold. Firstly, for a series of related monomers and their corresponding trimers we provided detailed information on the amount of charge that is transferred upon excitation and on the charge transfer excitation length. Secondly, for the same series of monomers we examined the question whether embedding effects influence the trend that was found in vacuum for the vertical exciton binding energy. Thirdly, we answered the question whether a relation exists between the binding energies of local and CT excitons for the series of related monomers.

By studying a plot of the electron density displacement upon excitation, the amount of charge transfer upon excitation, and the charge transfer excitation length, detailed and complementary information about the excitation process can be obtained. For the studied monomeric and trimeric systems, such a detailed study of the excitation process reveals that the thiophene unit – often included in the donor-acceptor co-polymer design to make the backbone more planar – actively participates in the charge transfer process and that its contribution can be tuned by choosing a particular push-pull group substitution pattern.

For all monomers, a reasonably similar decrease in the vertical local exciton binding energy was found with increasing static dielectric constant. This result was rationalised by noting that the electron density displacement upon excitation and the Mulliken charge difference between excited and ground state for the monomers are also reasonably similar, leading to a comparable interaction with the environment. So for these systems embedding effects do not change the trend that was found in vacuum for the vertical local exciton binding energy.

For the studied monomers, no relation exists between the vertical binding energy of the local exciton and of the CT exciton. This outcome can be understood because the variation in vertical local exciton binding energy depends mainly on the variation in vertical electron affinity between the monomers, which does not affect in a direct way the vertical CT exciton binding energy.

This work gives some interesting insights that may be useful for future development of promising OPV materials. First of all, it indicates that the thiophene unit actively participates in the charge transfer process and that its contribution can be tuned by choosing a particular push-pull group substitution pattern. Secondly, for polymers having a low exciton binding energy due to a high electron affinity this work shows that no interplay exists between intra- and inter-molecular CT states in the charge separation process in OPV devices through their binding energies.

ASSOCIATED CONTENT

Supporting Information. The vertical local exciton binding energy and dipole moment change upon excitation for monomers 1-6 and their corresponding trimers T1-T6, the vertical first excited state energy and difference between the Mulliken charges of the first excited and ground state for monomer 1 obtained with different quantum chemical methods and basis sets, and several excited state properties of monomers 1-6.

ACKNOWLEDGEMENTS

Prof. dr. J. C. Hummelen of the University of Groningen is thanked for stimulating discussions. R.W.A.H. acknowledges the Zernike Institute for Advanced Materials (“Dieptestategie” program) for financial support. This work is part of the research programme of the Foundation of Fundamental Research on Matter (FOM), which is part of the Netherlands Organisation for Scientific Research (NWO). This is a publication of the FOM-focus Group ‘Next Generation Organic Photovoltaics’, participating in the Dutch Institute for Fundamental Energy Research (DIFFER). The work was partially completed with computing time at the Dutch National Supercomputer Cartesius (SURFsara, SH-213-13).
REFERENCES

and exciton/charge transfer dynamics in a highly efficient semiconducting copolymer, “-pull group substituion, -transfer excitations,”

1-acceptor co

UK electronic structure package: algorithms, developments and


Table of Contents

Table S1. The vertical local exciton binding energy and dipole moment change upon excitation for monomers 1-6 and their corresponding trimers T1-T6.

Table S2. The vertical first excited state energy and difference between the Mulliken charges of the first excited and ground state, grouped per segment, for monomer 1 obtained with different quantum chemical methods and basis sets.

Table S3. The vertical first excited state energy, oscillator strength, HOMO energy, LUMO energy, orbital energy difference between HOMO and LUMO, vertical ionisation potential, and vertical electron affinity for monomers 1-6.
Table S1. The vertical local exciton binding energy \((E_b^{\text{exc}})_{\text{vert}}, \text{eV}\) and dipole moment change upon excitation \((\Delta \mu_{\text{ge}}, \text{Debye})\) for monomers 1-6 and their corresponding trimers T1-T6 from ref. 1.

<table>
<thead>
<tr>
<th>monomer</th>
<th>((E_b^{\text{exc}})_{\text{vert}})</th>
<th>(\Delta \mu_{\text{ge}})</th>
<th>trimer</th>
<th>((E_b^{\text{exc}})_{\text{vert}})</th>
<th>(\Delta \mu_{\text{ge}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.70</td>
<td>11.11</td>
<td>T1</td>
<td>1.91</td>
<td>2.14</td>
</tr>
<tr>
<td>2</td>
<td>2.61</td>
<td>11.53</td>
<td>T2</td>
<td>1.81</td>
<td>3.77</td>
</tr>
<tr>
<td>3</td>
<td>2.79</td>
<td>10.13</td>
<td>T3</td>
<td>1.92</td>
<td>4.14</td>
</tr>
<tr>
<td>4</td>
<td>2.46</td>
<td>17.84</td>
<td>T4</td>
<td>1.85</td>
<td>2.78</td>
</tr>
<tr>
<td>5</td>
<td>2.42</td>
<td>17.57</td>
<td>T5</td>
<td>1.72</td>
<td>3.79</td>
</tr>
<tr>
<td>6</td>
<td>2.73</td>
<td>13.47</td>
<td>T6</td>
<td>1.95</td>
<td>2.54</td>
</tr>
</tbody>
</table>

Table S2. The vertical first excited state energy \((S_1, \text{eV})\) and difference between the Mulliken charges of the first excited and ground state, grouped per segment, for monomer 1 obtained with different quantum chemical methods and basis sets (SP = state specific, SA = state average).

<table>
<thead>
<tr>
<th>Method</th>
<th>(S_1) (eV)</th>
<th>Mulliken charge difference (Exc-Gr)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TD-DFT (BHandH/6-31G**)</td>
<td>2.90</td>
<td>donor</td>
<td>0.19</td>
<td>0.08</td>
<td>-0.27</td>
</tr>
<tr>
<td>SP CASSCF (6-31G**)</td>
<td>4.23</td>
<td>thiophene unit</td>
<td>0.15</td>
<td>0.28</td>
<td>-0.43</td>
</tr>
<tr>
<td>SA CASSCF (6-31G**)</td>
<td>4.15</td>
<td>acceptor</td>
<td>0.06</td>
<td>0.30</td>
<td>-0.36</td>
</tr>
<tr>
<td>SP CASSCF (ANO-S)</td>
<td>3.89</td>
<td></td>
<td>0.17</td>
<td>0.30</td>
<td>-0.47</td>
</tr>
<tr>
<td>SA CASSCF (ANO-S)</td>
<td>3.74</td>
<td></td>
<td>0.13</td>
<td>0.36</td>
<td>-0.49</td>
</tr>
<tr>
<td>SP CASPT2 (ANO-S)</td>
<td>3.08</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SA CASPT2 (ANO-S)</td>
<td>3.09</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table S3. The vertical first excited state energy \((S_1, \text{eV})^*\), oscillator strength \((f)\), HOMO energy \((\varepsilon_{\text{HOMO}}, \text{eV})\), LUMO energy \((\varepsilon_{\text{LUMO}}, \text{eV})\), orbital energy difference between HOMO and LUMO \((\Delta \varepsilon_{\text{HL}}, \text{eV})\), vertical ionisation potential \(((\text{IP})_{\text{vert}}, \text{eV})\), and vertical electron affinity \(((\text{EA})_{\text{vert}}, \text{eV})\) for monomers 1-6 from ref. 1.

<table>
<thead>
<tr>
<th>monomer</th>
<th>(S_1) (eV)</th>
<th>(f)</th>
<th>(\varepsilon_{\text{HOMO}})</th>
<th>(\varepsilon_{\text{LUMO}})</th>
<th>(\Delta \varepsilon_{\text{HL}})</th>
<th>((\text{IP})_{\text{vert}}) (eV)</th>
<th>((\text{EA})_{\text{vert}}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.90</td>
<td>0.803</td>
<td>-5.72</td>
<td>-1.44</td>
<td>4.28</td>
<td>6.33</td>
<td>0.72</td>
</tr>
<tr>
<td>2</td>
<td>2.41</td>
<td>0.581</td>
<td>-5.74</td>
<td>-1.98</td>
<td>3.75</td>
<td>6.30</td>
<td>1.29</td>
</tr>
<tr>
<td>3</td>
<td>2.36</td>
<td>0.373</td>
<td>-5.85</td>
<td>-2.00</td>
<td>3.85</td>
<td>6.44</td>
<td>1.28</td>
</tr>
<tr>
<td>4</td>
<td>2.61</td>
<td>0.520</td>
<td>-5.86</td>
<td>-2.13</td>
<td>3.73</td>
<td>6.46</td>
<td>1.40</td>
</tr>
<tr>
<td>5</td>
<td>2.37</td>
<td>0.473</td>
<td>-5.64</td>
<td>-2.16</td>
<td>3.48</td>
<td>6.23</td>
<td>1.44</td>
</tr>
<tr>
<td>6</td>
<td>2.87</td>
<td>0.725</td>
<td>-5.69</td>
<td>-1.53</td>
<td>4.16</td>
<td>6.36</td>
<td>0.76</td>
</tr>
</tbody>
</table>

* These excitations all correspond to a HOMO \(\rightarrow\) LUMO transition \((c^2 > 0.83)\)

REFERENCES