A Promising Strategy to Improve Charge Separation in Organic Photovoltaics: Installing Permanent Dipoles in PCBM Analogues

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ABSTRACT

A multidisciplinary approach involving organic synthesis and theoretical chemistry is applied to investigate a promising strategy to improve charge separation in organic photovoltaics: installing permanent dipoles in fullerene derivatives. Firstly, a PCBM analogue with a permanent dipole in the side-chain (PCBDN) and its reference analogue without a permanent dipole (PCBBz) were successfully synthesised and characterised. Secondly, a multiscale modelling approach was applied to investigate if a PCBDN environment around a central donor-acceptor complex indeed facilitates charge separation. Alignment of the embedding dipoles in response to charges present on the central donor-acceptor complex enhances charge separation. The good correspondence between experimentally and theoretically determined electronic and optical properties of PCBDN, PCBBz and PCBM indicates that the theoretical analysis of the embedding effects of these molecules gives a reliable expectation for their influence on the charge separation process at a microscopic scale in a real device. This work suggests the following strategies to improve charge separation in organic photovoltaics: installing permanent dipoles in PCBM analogues and tuning the concentration of these molecules in an organic donor/acceptor blend.

1. INTRODUCTION

Organic photovoltaics (OPV) is an attractive renewable energy technology because cheap and abundant materials as well as low-cost and large-scale fabrication methods, *e.g.*, roll-to-roll printing, can be applied. However, the usefulness of this energy technology becomes questionable when one considers the typical power conversion efficiency (PCE) of $\sim 5\%$ of square meter sized panels and the short operational lifetime of 5 years under outdoor conditions. Still, OPV has significant advantages compared to other renewable energy technologies, like an energy payback time of less than a few months, energy return factors of more than 100, and ultrafast manufacture of a given energy producing unit.¹ Therefore, according to Jørgensen *et al.*¹, OPV technology is already competitive with other solar cell technologies.

To understand why the PCE of organic thin-film single junction solar cells is quite low (highest confirmed value for a research cell of 1-cm^2 area is $\sim 10\%$)², we need to know in detail their working mechanism. Bulk heterojunction solar cells are composed of a hole-conducting donor (typically a conjugated polymer) and electron-conducting acceptor material (usually a fullerene derivative).³ The commonly accepted scheme of the working mechanism consists of the following steps: light absorption by (mainly) the donor or the acceptor leading to the formation of local excitons, diffusion of these excitons towards the donor-acceptor interface, electron or hole transfer between the donor and the acceptor, transport of free charges to the electrodes and finally, charge collection.⁴ However, the generation of free charges has not been fully understood, since many experimental studies⁵⁻⁸ demonstrate the presence of a charge-transfer (CT) state at the donor-acceptor interface, an intermediate state between the initially excited state and final charge-separated (CS) state.^{4, 9-12} Loi *et al.*⁶ define

the CT state as a correlated electron-hole state, where the electron is located at a neighbouring molecule of the one where the hole is located.

An electronic state diagram illustrating the solar energy conversion to free charges is shown in Figure 1. Often the lowest CT (CT_1) state of the CT manifold is lower in energy than the CS state, which limits the generation of free charges. The energy difference is called the charge-transfer exciton binding energy (E_b^{CT}) and is estimated to be of 0.3-0.5 eV⁹. Several options have been proposed to explain how the charge generation process at the donor-acceptor interface can overcome this high E_b^{CT} . One of the most considered options assumes that excess photon energy leads to hot CT states that assist in charge separation.¹³⁻¹⁴ Recently, an experimental study performed by Vandewal *et al.*⁸ questions this proposal by revealing that the best materials systems show an internal quantum efficiency higher than 90% without the need for excess electronic or vibrational energy.

Figure 1. Electronic state diagram of the OPV working mechanism. 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_n). The green arrow shows the energy difference defined as the charge-transfer exciton binding energy labelled E_b^{CT} . Vibrational energy levels within the CT manifold are depicted in grey. Higher energy electronic D^* states, as well as electronic acceptor excited states, are omitted for clarity. (D^* = donor excited state, $D^{+\bullet}$ = radical cation of donor, $A^{-\bullet}$ = radical anion of acceptor)

Another option was given by Arkhipov *et al.*¹⁵ who suggest the assistance of an interfacial dipolar layer in the exciton dissociation process at a polymer/acceptor interface. Due to partial charge transfer between the polymer and the acceptor in the dark an interfacial dipole is formed, which creates a repulsive potential barrier for the hole on the polymer preventing recombination with the electron on the acceptor. Their proposed model¹⁵ makes use of a parabolic (harmonic) approximation for the electrostatic potentials and assumes that the polymer chains are positioned parallel to the interface. Koehler *et al.*¹⁶ extended the model of Arkhipov *et al.*¹⁵ by allowing disorder in the position of the interfacial dipoles and, recently, Wiemer *et al.*¹⁷ extended the model even further by going beyond the harmonic approximation. Computational support for the model was given by Marchiori *et al.*¹⁸⁻¹⁹ who concluded for isolated P3HT/C₆₀ and P3HT/[60]PCBM-like complexes that an interfacial dipole exists. Several experimental results²⁰⁻²² suggest that a dipolar layer can be formed at donor/acceptor interfaces.

The increase in entropy (ΔS) when charges move away from each other is also proposed to be essential for charge separation.²³ Clarke *et al.*²³ showed quantitatively that for equilibrium processes the contribution from ΔS can substantially decrease the Coulomb barrier for charge separation. However, Gregg²⁴ states that for non-equilibrium processes like an illuminated solar cell, the magnitude of entropic effects should diminish considerably compared to equilibrium processes. Considerations of ΔH are still useful for studying charge separation processes because an entropy contribution is expected to stabilise the CS state relative to the CT state leading to an additional decrease in E_b^{CT} . In short, the question on how the charge generation process can overcome the high E_b^{CT} has so far been unanswered.

One way to lower the Coulomb attraction between charges is to increase the dielectric screening of organic donor and acceptor materials. Recently, Koster *et al.*²⁵ showed that the key parameter for enabling PCEs of OPV of more than 20% is the relative dielectric constant

(ϵ_r). According to classical descriptions like the Debye and Clausius-Mossotti equations, this bulk property is related to the properties of its constituting molecules/atoms. The Debye equation illustrates that three different microscopic mechanisms of polarisation can exist in a dielectric material: the electronic, distortion and orientation polarisation. The last one only exists for polar molecules. The Clausius-Mossotti equation is the same expression as the Debye equation but without this permanent dipole contribution.²⁶

However, as Heitzer *et al.*²⁷ indicate, these equations are inappropriate for many materials, especially for molecule-based systems. Therefore these classical descriptions should rather be used as guidelines to understand the origin of dielectric response at the molecular scale. So increasing the relative dielectric constant might be achieved by increasing the electronic polarisation, *i.e.*, the polarisability, and/or by increasing the orientation polarisation of donor and acceptor molecules (by incorporating dipoles in these molecules). Thus, apart from optimising molecular properties like relative alignments of frontier molecular orbital energies in order to improve the OPV efficiency, another strategy^{25, 28-30} is to install polarisable side-groups and permanent dipoles in conjugated polymers and fullerene derivatives in order to facilitate charge generation. Ideally, the electronic, optical and solubility properties of the molecules should not change.²⁹

Several promising first steps to investigate this strategy have recently been reported. Jahani *et al.*²⁹ describe an increase in ϵ_r of fulleropyrrolidines with triethylene glycol monoethyl ether (TEG) side-chains ($\epsilon_r \approx 5.5$) and the excellent solubility of these functionalised fullerenes in organic solvents without any significant changes in electron mobility, UV-vis absorption and electrochemical properties. Torabi *et al.*³⁰ report about impressive doublings of ϵ_r up to ~ 5 -6 for poly(*p*-phenylene vinylene) and diketo-pyrrolopyrrole based polymers also functionalised with TEG side-chains. Donaghey *et al.*³¹ synthesised two non-fullerene acceptors with short ethylene glycol chains and measured an enhancement in the dielectric

constant (up to 9.8) compared to their alkylated counterparts, while the optical and electrochemical properties and electron mobilities did not change.

Application of donor and acceptor molecules functionalised with TEG side-chains in real OPV devices is expected to result in higher PCEs. Loss processes that originate from Coulomb interactions between charges are not beyond the ns time scale, which means that an enhancement of ϵ_r up to frequencies of 10^9 Hz, *i.e.*, GHz, can diminish these loss processes. Due to the flexibility and swiftness of these TEG side-chains, reorientations of their dipoles, *i.e.*, orientation polarisation, can potentially increase ϵ_r in the GHz range and diminish loss processes leading to higher PCEs.³⁰ Studies of the performance of OPV devices containing donor and acceptor molecules functionalised with TEG side-chains²⁹⁻³⁰ are currently in progress. Donaghey *et al.*³¹ report some encouraging outcomes of initial OPV device testing. Application of their synthesised high dielectric constant non-fullerene acceptors with P3HT as donor in an OPV device resulted in a slight enhancement in the short-circuit current. Further study is required to disentangle whether the improvement in the OPV device performance is due to the increase in the dielectric constant or due to other factors like changes in the blend morphology.³¹

In this work, we focus on installing permanent dipoles in [6,6]-phenyl-C₆₁-butyric acid methyl ester ([60]PCBM, labelled PCBM from now on, Figure 2) analogues in order to facilitate charge separation. Our theoretical model system consisted of a central donor-acceptor complex embedded in only PCBM analogues with a permanent dipole in the side-chain. We concentrate on the embedding effects of these dipoles, being part of the molecular environment of the central donor-acceptor complex, on charge separation. We focus on PCBM analogues, since the majority of OPV devices uses [60]PCBM and [70]PCBM as electron acceptors, because of their ability to easily accept electrons, to obtain favourable nanoscale morphology, to support electron transport in three dimensions, and their reasonably

good electron mobilities.³² In reality, the environment around a donor-acceptor complex also contains polymers, because an environment of solely polymers or PCBM makes good charge conduction impossible. It is shown²⁸ that an embedding of solely monomers could facilitate charge separation only when permanent dipoles are installed in the side-chains. Additionally, these dipoles have to be sufficiently large and able to rotate modestly.²⁸ For monomer/PCBM mixed environments, the stabilising effect is less compared to “pure” embeddings where a maximum stabilising effect resulting from the constituting molecules is calculated.

The importance of a multidisciplinary approach involving materials science, (theoretical) chemistry and (theoretical) physics to provide understanding of the OPV working mechanism and to achieve highly efficient solar cells in future, has already been underlined in several studies.^{11, 33} In this work, we apply this multidisciplinary approach. Firstly, we synthesised and characterised a PCBM analogue with a permanent dipole in the side-chain called [6,6]-phenyl-C₆₁-butyric acid 2-dimethylamino-5-nitrobenzyl ester (PCBDN, Figure 2) and its reference analogue without a permanent dipole called [6,6]-phenyl-C₆₁-butyric acid benzyl ester (PCBBz, Figure 2). Secondly, we used electronic structure theory to predict the potential effect of reorientations of these dipoles on charge separation in OPV. Due to the large system size, theoretical modelling is challenging¹⁰ and therefore the current strategy³³ is to combine macroscale modelling molecular dynamics (MD) with quantum chemical (QC) calculations on the molecular scale. Usually Density Functional Theory (DFT) is applied because this method provides the required accuracy and is computationally feasible. This combined MD/QC approach is also applied here.

Figure 2. Chemical structures of PCBM, PCBDN, PCBBz and Si-CPDTBT.

2. METHODS

2.1. Synthetic procedure

2.1.1. General procedure for the synthesis of PCBDN

The synthetic route to prepare PCBDN (Figure 2) is shown in Scheme S1 in the Supporting Information. The substitution reaction of 2-chloro-5-nitrobenzaldehyde (**1**) with dimethylamine afforded the corresponding benzaldehyde (**2**) in quantitative yield. The aldehyde was efficiently reduced to alcohol (**3**) using sodium borohydride. The target methanofullerene PCBDN (**4**) was prepared by a transesterification reaction of PCBM with alcohol (**3**) in ODCB at 110°C in 57% yield. Experimental details of the materials synthesis are presented in the Supporting Information. Structures of the synthesised compounds were confirmed by analytical and spectroscopic data, which are also presented in the Supporting Information.

2.1.2. General procedure for the synthesis of PCBBz

The synthetic route to prepare PCBBz (Figure 2) is shown in Scheme S1 in the Supporting Information. PCBBz (**6**) was synthesised from [60]PCBM and benzylalcohol (**5**) by transesterification in 63% yield. Experimental details of the materials synthesis are presented in the Supporting Information. Structures of the synthesised compounds were confirmed by analytical and spectroscopic data, which are also presented in the Supporting Information.

2.2. Computational procedure

Geometries of PCBDN, PCBBz and PCBM (Figure 2) were optimised using DFT (B3LYP³⁴/6-31G**) with the program GAMESS-UK³⁵. Subsequently, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of these molecules were calculated using DFT (BHandH³⁶/DZP) and the lowest 60 vertical excitation energies were calculated using time-dependent DFT (TD-DFT) (BHandH/DZP) with ADF³⁷⁻³⁸.

Isotropic polarisabilities and dipole moments of PCBDN, PCBBz and PCBM were calculated using DFT (B3LYPg/aug-cc-pVDZ) with the program DALTON³⁹ (see Figure S3 in the Supporting Information for the dipole moment of these molecules).

To model the effect of the molecular environment on charge separation in OPV, we followed our recently developed procedure²⁸. MD simulations (NVT) with the program Tinker⁴⁰ were performed for generating configurations of an embedding of either PCBDN or PCBBz around a (geometry optimised) central donor-acceptor complex consisting of one monomer of a typical donor-acceptor co-polymer called poly[(4,4'-bis(2-heptyl)dithieno[3,2-*b*:2',3'-*d*]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] (Si-

PCPDTBT and its monomer Si-CPDTBT) and PCBDN (see Figure S3 in the Supporting Information for its optimised structure and dipole moment). The atoms of the central donor-acceptor complex were set inactive during the MD simulation. In view of computational efficiency we used a monomer instead of an oligomer. Using a monomer instead of an oligomer does not affect our qualitative conclusions that are related to the embedding effects, although the embedding effects may be smaller when considering an oligomer.

Subsequently, QC calculations using (TD-)DFT (BHandH/DZP) with the program ADF of the central complex both without and with environment were performed. Two different embeddings were investigated: one consisting of PCBDN and one consisting of PCBBz. The influence of the PCBDN or PCBBz environment on the excitation, CT and CS state energies of the central donor-acceptor complex was accounted for by using the Discrete Reaction Field (DRF) method⁴¹⁻⁴³. This method is a QM/MM approach that treats the central complex using a quantum chemical approach (QM) and the PCBDN or PCBBz embedding molecules with point charges and polarisabilities (MM). According to Van Duijnen *et al.*⁴⁴, a full treatment of all interactions on a microscopic scale is needed to correctly describe the early stages of charge dissociation of the local and CT excitons. Therefore a discrete solvation model instead of a continuum solvation model is used. In order to study the effect of reorientations (or alignment) of embedding dipoles in response to charges present on the central complex, the embedding is dynamic³³, *i.e.*, changes that occur in the environment upon electron transfer were taken into account. Computational details of the complete procedure are reported in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Comparison between experimental and calculated electronic and optical properties

The electrochemistry of fullerenes is one of their most important properties as conjugated materials. Therefore we investigated the electrochemical properties of PCBDN, PCBBz and PCBM by cyclic voltammetry. Table 1 gives an overview of these electrochemical properties together with calculated HOMO and LUMO energies. The measured half-wave potentials of the reduction processes of all compounds are listed.

Table 1. Electrochemical properties* (V) and calculated HOMO and LUMO energies (eV) of PCBDN, PCBBz and PCBM

Compound	$E_{1/2}$ 1, red	$E_{1/2}$ 2, red	HOMO	LUMO
PCBDN	-1.089	-1.482	-7.92	-3.88
PCBBz	-1.095	-1.489	-7.90	-3.86
PCBM	-1.097	-1.487	-7.87	-3.83

* Experimental conditions: Bu_4NPF_6 (0.1 M) as the supporting electrolyte; ODCB/ CH_3CN (4:1) as solvent; Pt, working electrode; Pt wire, counter electrode; Ag/AgCl, reference electrode; scan rate 10 mV/s; potentials are relative to ferrocene/ferrocene⁺.

The computational results show that the LUMO energies and the HOMO-LUMO energy differences are similar for these compounds. These findings are in agreement with the experimental data, which show that the differences in the first and second reduction potentials are very small, indicating that the behaviour of the reduction potential is not affected by the dipoles. So installing a permanent dipole in the side-chain of a PCBM

analogue does not modify its π -conjugated system, which is one of the advantages of the strategy^{25, 28-30} of installing permanent dipoles in side-chains of conjugated polymers and fullerene derivatives in order to facilitate charge separation.

The measured and calculated UV-vis absorption spectra of PCBDN, PCBBz and PCBM (Figure 3) are very similar apart from an overestimation of the energies in the case of the calculated spectra. Therefore, all calculated spectra are shifted by 0.6 eV towards lower energies, *i.e.*, larger wavelengths. The optical properties of these molecules appear to be nearly similar so it can be concluded that installing a permanent dipole in the side-chain of a PCBM analogue does not affect its optical properties.

Figure 3. Experimental UV-vis absorption spectra (continuous curves) of PCBDN (blue), PCBBz (red) and PCBM (black) in 10^{-5} M CHCl_3 solution and calculated UV-vis absorption spectra (vertical lines) of PCBDN (blue), PCBBz (red) and PCBM (black) in vacuum. All calculated spectra are shifted by 0.6 eV to lower energy.

Based on the good correspondence between experimentally and theoretically determined electronic and optical properties of PCBDN, PCBBz and PCBM it is expected that the theoretical analysis of the embedding effects of these molecules (see section 3.3) gives a

reliable expectation for their influence on the charge separation process at a microscopic scale in a real device.

3.2. Calculated isotropic polarisabilities and dipole moments

Table 2 gives an overview of the calculated isotropic polarisabilities and dipole moments of PCBDN, PCBBz and PCBM (see Figure S3 in the Supporting Information for the dipole moment of these molecules). The isotropic polarisability per electron is similar for PCBDN (548 electrons), PCBBz (502 electrons) and PCBM (462 electrons). Therefore a similar optical dielectric constant (dielectric constant at optical frequencies, *i.e.*, only electronic polarisation defines ϵ_r) is expected for these systems. When the additional screening from dipoles is considered too, a larger screening is expected for a PCBDN embedding compared to its reference, a PCBBz embedding, due to the larger dipole moment of PCBDN. This hypothesis is tested in the following theoretical analysis (see section 3.3). When both newly synthesised PCBM analogues are compared to PCBM, it appears that the dipole moment of PCBDN is larger and the dipole moment of PCBBz smaller than the one of PCBM.

Table 2. Calculated isotropic polarisabilities (a.u.) and dipole moments (Debye) of PCBDN, PCBBz and PCBM.

Compound	Polarisability	Polarisability per electron	Dipole moment
PCBDN	838.79	1.53	5.97
PCBBz	784.54	1.56	2.35
PCBM	716.44	1.55	4.01

3.3. Calculated electronic state diagrams

Application of the computational procedure described in paragraph 2.2 resulted in electronic state diagrams as presented in Figure 4 for the studied donor-acceptor complex Si-CPDTBT-PCBDN in vacuum (Figure 4a), Si-CPDTBT-PCBDN embedded in PCBBz (Figure 4b) and Si-CPDTBT-PCBDN embedded in PCBDN (Figure 4c). Figure 4d shows a particular snapshot of a MD simulation on which the QM/MM approach is applied (QM part: red, MM part: blue). $(S^*)_{\text{vert}}$ corresponds to the excited state that has the largest oscillator strength, $(CT)_{\text{vert}}$ to the excited state with the largest charge-transfer character from Si-CPDTBT to PCBDN, and $(CS)_{\text{vert}}$ to the charge-separated state, all three at the ground state geometry of the complex. See Table S1 in the Supporting Information for more details on the labelling of these states and on the occupied-virtual orbital pairs that contribute most to these excitations. $(CS)_{\text{relaxed}}$ corresponds to the charge-separated state determined with the relaxed cationic and anionic complex geometries. $(CS)_{\text{relaxed}}$ without dipole alignment is determined without taking into account the response of the embedding dipoles to net charges present at the central donor-acceptor complex, so in this case the embedding dipoles are oriented randomly. $(CS)_{\text{relaxed}}$ with dipole alignment takes into account the response of these dipoles to charges present on the central donor-acceptor complex, so in this case the embedding dipoles are allowed to align favourably.

Figure 4. Electronic state diagrams (**a**, **b**, **c**) for the studied donor-acceptor complex Si-CPDTBT-PCBDN. Diagram (**a**) shows the results for Si-CPDTBT-PCBDN in vacuum, (**b**) for Si-CPDTBT-PCBDN embedded in PCBBz, and (**c**) for Si-CPDTBT-PCBDN embedded in PCBDN. Black lines correspond to vertical excitations, *i.e.*, energies obtained at the ground state geometry of Si-CPDTBT-PCBDN. Red and blue lines correspond to energies obtained at relaxed cationic and anionic geometries of Si-CPDTBT-PCBDN. The red line corresponds to the CS state without dipole alignment and the blue line to the CS state with dipole alignment. (**d**) shows a particular snapshot of a MD simulation on which the QM/MM approach is applied. The central complex (QM) is depicted in red and the embedding molecules (MM) in blue.

Figure 4a-c show that due to the environment (either PCBBz or PCBDN) $(CS)_{\text{vert}}$ is stabilised by ~ 1.5 eV. $(S^*)_{\text{vert}}$ nor $(CT)_{\text{vert}}$ are significantly affected by the molecular environment.

For Si-CPDTBT-PCBDN in vacuum and embedded in PCBDN, geometry relaxation of the CS state leads to a stabilising effect of ~ 0.5 eV (Figure 4a and 4c). This lowering originates predominantly from relaxation of the cation and results in a significant decrease in the ionisation potential (IP, Table 3). The stabilising effect due to geometry relaxation is smaller for Si-CPDTBT-PCBDN embedded in PCBBz, namely ~ 0.1 eV (Figure 4b), due to a much smaller relaxation of the cation (Table 3). A slightly unfavourable environment around Si-CPDTBT-PCBDN might cause this apparent smaller stabilising effect of geometry relaxation (see Supporting Information for computational details).

Inclusion of alignment of embedding dipoles in response to charges present on Si-CPDTBT-PCBDN results in an extra stabilisation of the CS state, which is significantly larger in the case of the PCBDN environment compared to the PCBBz environment (Figure 4b and 4c). For the PCBDN environment, dipole alignment results in an extra stabilisation of ~ 1.4 eV. This stabilising effect is the largest for the cation, resulting in a significant lowering of its IP (Table 3). For the PCBBz environment, dipole alignment results in an extra stabilisation of only ~ 0.6 eV. However, in this case, the overall CS state stabilisation of ~ 0.7 eV due to geometry relaxation and dipole alignment together is a better aspect to look at, since the effect of geometry relaxation is probably slightly underestimated, as explained previously.

To corroborate that indeed aligned dipoles in the embedding cause the significant lowering in IP, the dipole moments of the PCBDN embedding were “turned off” by making all charges of the embedding atoms equal to zero. In this way, the embedding configuration did not change and kept its dielectric screening from polarisability, but the additional screening from

dipoles was removed. This procedure shows that the IP recovers to the value of ~ 6 eV, *i.e.*, the one for Si-CPDTBT-PCBDN embedded in PCBBz (Table 3). This outcome is in agreement with the similar polarisabilities per electron of PCBDN and PCBBz (Table 2).

Table 3. Calculated ionisation potentials (IP, eV), electron affinities (EA, eV) and CT exciton binding energies (E_b^{CT} , eV) for the systems under study

System	(CS) _{vert}		(CS) _{relaxed} without dip. alignm.		(CS) _{relaxed} with dip. alignm.		E_b^{CT} with respect to (CS) _{relaxed}	
	IP	EA	IP	EA	IP	EA	without dip. alignm.	with dip. alignm.
Si-CPDTBT-PCBDN in vacuum	6.8	2.8	6.3	2.7	-	-	1.3	-
Si-CPDTBT-PCBDN in PCBBz	6.1	3.5	5.9	3.4	5.7	3.8	0.2	-0.4
Si-CPDTBT-PCBDN in PCBDN	5.4	3.0	4.7	2.8	3.6	3.1	-0.5	-1.9

Table 3 contains the calculated IP and electron affinity (EA) obtained from the single-point DFT (BHandH/DZP) calculations performed on the optimised neutral, cationic and anionic DFT (B3LYP/6-31G**) geometries. As expected, due to geometry relaxation of Si-CPDTBT-PCBDN its IP decreases. However, the decrease shown for EA is unphysical and

caused by the change in basis set and functional. The DFT (B3LYP/6-31G**) calculations show a small relaxation of the anion, and a corresponding small increase in EA (see Table S2 in the Supporting Information).

Table 3 also gives an overview of E_b^{CT} , defined previously as the energy difference between $(CS)_{relaxed}$ and $(CT)_{vert}$. This energy difference, when positive, limits the generation of free charges. In Table 3 this difference is calculated with respect to $(CS)_{relaxed}$ without and with dipole alignment. For both embeddings E_b^{CT} is negative when the effects of the environment, geometry relaxation and dipole alignment on the CS state energy are considered. In these situations free charge generation is favourable. When the effect of dipole alignment is excluded, only for Si-CPDTBT-PCBDN embedded in PCBDN $(CS)_{relaxed}$ is still below $(CT)_{vert}$, although for Si-CPDTBT-PCBDN embedded in PCBBz this probably also holds. But due to the underestimated effect of geometry relaxation explained previously, the value of E_b^{CT} is positive. When one considers the expected stabilisation of ~ 0.5 eV caused by geometry relaxation, $(CS)_{relaxed}$ without dipole alignment of Si-CPDTBT-PCBDN embedded in PCBBz will be ~ 2.1 eV and consequently the value of E_b^{CT} will be negative too (~ -0.2 eV).

These results suggest that an environment of solely PCBBz around a Si-CPDTBT-PCBDN complex already favours free charge generation in OPV. In reality, the environment around a donor-acceptor complex also contains polymers. For an environment consisting of solely monomers with sufficiently large dipoles in the side-chains²⁸ the stabilising effect due to dipole alignment appears to be smaller compared to an environment consisting of solely PCBM analogues with a dipole in the side-chain. Therefore, for monomer/PCBM mixed environments the stabilising effect is less compared to the (maximum) stabilising effect that was found for the fullerene-rich environments studied here.

In this respect, this work leads to promising strategies for improving charge separation in OPV by optimising the molecular environment: installing permanent dipoles in PCBM analogues, and tuning the concentration of these molecules in the blend. In order to facilitate charge separation in OPV, both the magnitude of the installed dipoles in PCBM analogues (and/or polymers) and the concentration in the active layer of these molecules with a permanent dipole in the side-chain can be used as a parameter to tune the dielectric screening of the environment in such a way that E_b^{CT} becomes negative. One could even think of a third tuning parameter to optimise the molecular environment for charge separation: mixing PCBM with, in this case, PCBDN to form the electron-conducting phase of an organic donor/acceptor blend.

We can make an analogy between our theoretical system of a donor-acceptor complex embedded in a fullerene-rich environment and an experimental situation with an increased PCBM concentration in the organic donor/acceptor blend. In several studies^{6, 45} where the effect of increased PCBM concentration was investigated, a red shift on CT emission was measured. This was explained by suggesting that adding more PCBM leads to a reduction of the Coulomb attraction between electrons and holes (due to an increased average dielectric constant of the medium). Our calculations can be regarded as modelling the dielectric screening of a PCBM-like embedding on a microscopic scale of ~ 40 Å, *i.e.*, the size of the box filled with PCBBz or PCBDN, as Van Duijnen *et al.*⁴⁴ suggested. Our results corroborate the suggestion done in some experimental studies^{6, 45} that increasing the PCBM concentration in polymer/PCBM blends facilitates charge separation in organic solar cells because of the more polarisable medium.

The effect of dipole reorientations on other aspects - besides charge separation - that determine the overall OPV efficiency, like charge transport and blend morphology, is subject of current studies. The encouraging initial results³¹ of the performance of OPV devices

containing organic molecules with permanent dipoles in their side-chains increase the future expectations for these materials.

4. CONCLUSIONS

This work illustrates using a multidisciplinary approach that the proposed strategy^{25, 28-30} for improving charge separation in OPV, *i.e.*, installing polarisable side-groups and permanent dipoles in polymers and PCBM analogues, is a promising one. The good correspondence between experimentally and theoretically determined molecular properties of the studied PCBM analogues indicates that the theoretical analysis of the embedding effects of these molecules gives a reliable expectation for their influence on the charge separation process at a microscopic scale in a real device.

The combination between experiment and theory is necessary in order to make a sound prediction of the effects that embedding dipoles might have on charge separation in OPV devices. Therefore, this work can be seen as one of the first studies providing a synthetic route for this new class of promising organic semiconductors, *i.e.*, PCBM analogues with a permanent dipole in the side-chain, and at the same time focusing on the effect of these functional materials on the charge separation process in organic solar cells.

Promising strategies for improving charge separation in OPV are provided. Besides the installation of dipoles and their magnitude, also the concentration of PCBM analogues with a permanent dipole in the side-chain in an organic donor/acceptor blend can be used to tune the dielectric screening of the environment. These insights may indicate directions in the search for better performing OPV devices.

The applied procedure for modelling charge separation at the microscopic level of OPV devices can be taken a step forward by increasing the part that is treated using a quantum chemical approach, *e.g.*, two PCBM molecules and a short oligomer. In this way the procedure can be used to study the effect of charge delocalisation on the excited state energies and the energies of the CT and CS states. Such a study is currently in progress. Several studies^{33, 46} have already mentioned this and other similar challenging directions for future research in multiscale modelling of OPV devices.

ASSOCIATED CONTENT

Supporting Information Available: Experimental details, synthetic routes, ¹H NMR spectra, computational details, figures illustrating the dipole moment of the studied systems, and additional Tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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