

# Investigation of functionalities for the monomer diphenyl-BDT for the purpose of increased solar energy performance.

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## 1 Abstract

Different functional groups were tested to improve the properties of diphenyl-benzodithiophene with connecting triethyl glycol chains for solar cell performance. This was done computationally using DFT geometry optimization and coupled perturbed Kohn-Sham calculations to compute the polarizability and dielectric constant of the adapted molecules and subsequently improve these. The dielectric constant is theorized to reduce the exciton binding energy which limits organic solar cell efficiency. [1] The polarizability is the molecular property related to the dielectric constant. The highest optical dielectric constant is achieved by extending the  $\pi$ -system to dinaphthyl-benzodithiophene with triethyl glycol chains, with an optical dielectric constant of 2.97.

It is shown that the dielectric constant can be predicted with calculated molecular polarizabilities using DFT and calculated molecular van der Waals volumes, and it is shown that the polarizability per molecular van der Waals volume can be predicted with the Hammett parameters of the functional groups.



## 2 Introduction

### 2.1 Organic Solar Cell Devices

To face the climate challenges of today, there is a need for sustainable energy. Solar energy could be a bountiful source of renewable energy with sufficiently effective and affordable solar cells. Where silicon-based solar cells are currently the industry standard solution, organic solar cells are an alternative, which could allow for new applications, to take advantage of their low production cost, low weight, and high flexibility. [2]

Most of the research on organic solar cell devices consider bulk heterojunction (BHJ) polymer solar cells with push-pull copolymers as a donor molecule, where a donor and an acceptor monomer are in an extended conjugated system. [3] One of the advantages of a copolymer over a homopolymer as a donor is the improved control over the band gap, allowing a reduction of the band gap to improve light absorption. The acceptor monomer of a copolymer has a lower HOMO and LUMO than the donor, allowing the extended conjugation of both monomers to have a HOMO with the character of the antibonding linear combination of both monomer HOMOs. The dominant contribution to this HOMO is of the donor monomer as a consequence. The LUMO of the copolymer, with the character of the bonding combination of the LUMO of both monomers, is dominated by the acceptor contribution. This strategy for the donor copolymer gives control over the band gap as the energy levels of donor and acceptor monomer dictate the HOMO and the LUMO respectively, and allows the band gap to be in the range where it accepts the

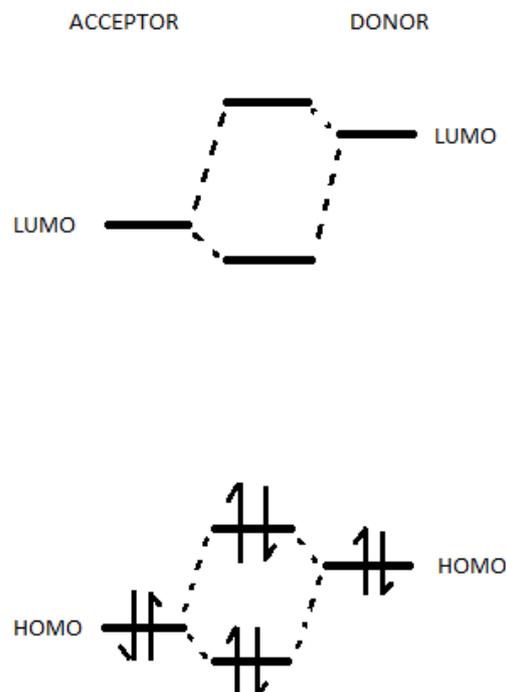


Figure 1: Schematic energy diagram of a donor-copolymer

energy of the sun efficiently, and also allows the energy level of the LUMO to line up with the acceptor of the BHJ to reduce the energy loss through heat. [4]

### 2.2 Diphenyl-Benzodithiophene

Benzodithiophene (BDT) is a popular donor monomer for copolymers [3]. It is a rigid planar molecule which forms planar copolymers. This is caused by the partially quinoidal nature of the bond between the BDT and the acceptor monomer through the conjugated system, and this also allows for a significant hole transporting ability and high carrier mobility [5] which gives BDT based copolymers good electrical prop-

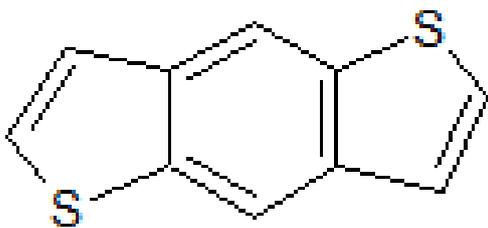


Figure 2: Benzodithiophene

erties. To further enhance the donating properties of BDT the related dithienyl benzodithiophene has also been studied extensively [6] [3]. As an alternative to this, diphenyl-benzodithiophene was studied here, because of the synthetic ease of functionalizing this phenyl group which could improve the properties and would improve the understanding of the monomer.

To further tune these donor copolymers used in BHJs, halogen functional groups have been used to lower the bandgap by disproportionately affecting the LUMO. Given the LUMO of the polymer is dominated by the acceptor monomer contribution, fluorine or chlorine are often successfully be applied to the acceptor monomers of such copolymers [7], though there are exceptions in which beneficial changes to the polymer were made by adding fluorine or chlorine to a donor monomer of these copolymers [8].

Both fluorine and chlorine lower the electron density of the polymer inductively through their electronegativity but donate to an aromatic  $\pi$ -system through their lone pair electrons. Fluorine is more effective as a  $\pi$ -donor as the orbitals match better to the carbon-based extended conjugated systems. [9] The electronegative contribution to the LUMO can be disproportionate

compared to the effect on the HOMO by these halogens, allowing control over the energy level of the molecule through the overall electron density, as well as the frontier orbitals formed by  $\pi$ -orbitals through their donating effects and through this these functional changes modulate the band gap. The LUMO contribution would predominantly be the acceptor monomer contribution, so to lower the band gap to increase light absorption the lowest unoccupied molecular orbital of the acceptor monomer would have to be lowered in energy level, either by lowering the overall electron density of the monomer or by lowering the energy level of the frontier orbitals. Chlorine and fluorine are common functional groups to modify the acceptor part of the copolymer [7], but there are exceptions where they are effective at modifying the donor monomer. [8] After being excited the electron is transferred from the donor copolymer to an acceptor and the LUMO energy levels have to be comparable to facilitate this transfer. Both chlorine and fluorine have seen successful usage to match the energy level of the copolymer to those of fullerene-based acceptors [8], as well as creating band gaps closer to the optimal value for sunlight absorption. [4].

Fluorine, chlorine and other functional groups would be used to attempt to improve the properties of diphenyl-benzodithiophene.

### 2.3 Exciton dissociation

After excitation by light, the excited electron and the associated hole are still localized in the same region. The positive and negative charge are a driving force

for charge recombination, lowering photovoltaic efficiency. This Coulomb attraction bound electron-hole pair, an exciton, would have to be dissociated fully to allow either charge carrier to move freely through the material, to allow for charge transfer allowing for a potential to arise over the cell [10].

Despite advancements within the paradigm of copolymers in recent years which have allowed top end organic photovoltaics to reach efficiencies up to 10%, these efficiencies compare unfavorably to the efficiencies of commercial silicon-based solar cells which achieve efficiencies of 15-20%. [3] Koster et al. showed that exciton binding energies would limit organic photovoltaic cell efficiency and that the exciton binding energy was dependent on the dielectric constant. [1].

A strategy to lower this exciton binding energy involves raising the dielectric constant, thereby reducing direct recombination but also related processes where recombination occurs with charge carriers of other molecules [11]. According to van der Horst et al. [12] this exciton binding energy is given by  $E_h\mu\epsilon^2$  with  $E_h\mu$  fitting parameters giving the hydrogen electron binding energy and a reduced mass. By raising the dielectric constant the exciton binding energy could be reduced sufficiently for it to be overcome by thermal energy alone, essentially freeing the electron to move throughout the material, eliminating the requirement of a bulk heterojunction for high solar cell efficiency. The gap between silicon (11.7 [13]) based solar cells and organic solar cells (2-4 [14]) could help explain the current difference in efficiency between these two approaches

to energy generation from sunlight. Here it was attempted to find a diphenyl-BDT related monomer with an improved dielectric constant.

The dielectric constant depends on molecular, electronic and nuclear contributions. The lifetime of the exciton is thought to be in the order of a nanosecond [11], which is in the range of molecular rotations and vibrations, while the process of excitation is in an optical timescale and the charge transfer to a fullerene-based acceptor is in the order of 40fs, the rapidity of which is core to the success of organic photovoltaics [?] as it allows the generation of a potential to compete with the electron-hole recombination and other competing decay processes. Would the lifetime of an excited state in a particular photoactive molecule be shorter, then the rotation of a dipole or the generation of a dipole through nuclear motion would insufficient to affect it before it decayed, and to replace the acceptor in a bulk heterojunction solar cell by having a sufficiently high dielectric constant, it would have to be comparably incentivizing as the charge transfer to an acceptor in a bulk heterojunction solar cell to prevent charge recombination. The electric component of the dielectric constant would act in a shorter timescale.

In light of the previous comparison with silicon-based solar cells, the dielectric constant of silicon is mainly the electronic contribution. [14] The focus here would be on improving the short timescale, electronic contribution to the dielectric constant for diphenyl-benzodithiophene.

## 2.4 Polarizability

The polarizability is the related molecular property to the dielectric constant of the material. Both describe the response to an applied electric field. The relation between the polarizability and the dielectric constant is [15]:

$$\epsilon_r = 1 + \frac{\epsilon_0 \alpha}{V} \quad (1)$$

While the polarizability  $\alpha$  is a tensor, the nature of polymers would be to randomly distribute themselves and as such the direction dependence would be the average.

The polarizability was calculated using the coupled perturbed Kohn-Sham method and to relate it to a dielectric constant, by the absence of a description of the volume in a material for most of the modeled alternative molecules, the molecular van der Waals volume was used. The polarizability divided by the molecular van der Waals volume would give an indication of what functional changes could give rise to a higher dielectric constant. To improve the dielectric constant of a material, the polarizability divided by the van der Waals volume for a molecule had to be improved.

## 2.5 Outset

The dihedral angle between the phenyl and BDT moiety in the model of the unmodified molecule was 59.8 degrees, where up to the order of 30 degrees it is still considered a conjugated system between two aromatic rings. [16] Further evidence was found in the bond length of this bond, at a length of 1.49 Å, closer to the expected bond length of a single carbon-carbon bond

(154Å) than to the aromatic expected bond length of 140Å. This limited communication through the  $\pi$ -system within the molecule would prevent a functional group attached to the phenyl moiety to affect the  $\pi$ -system in the molecule beyond that aromatic ring and would limit the ability of the functional group to change the properties of the entire monomer. A smaller dihedral angle could increase the size of the aromatic system as the connection between the phenyl and the BDT improved and allow for an increase in polarizability.

Further evidence of the limited communication between the distinct aromatic systems was found in the frontier orbitals of the reference molecule. The HOMO of the reference molecule could be seen as a anti-bonding combination of the BDT and methoxybenzene HOMOs, while the LUMO as the bonding combination of LUMO of the BDT and an unoccupied orbital of the methoxybenzene. For the isolated BDT,

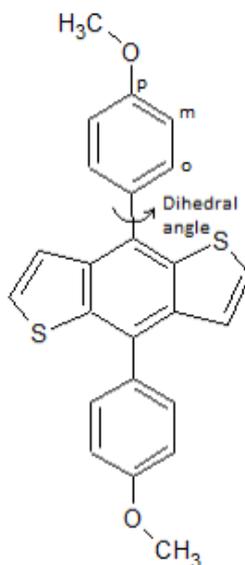


Figure 3: Base monomer model

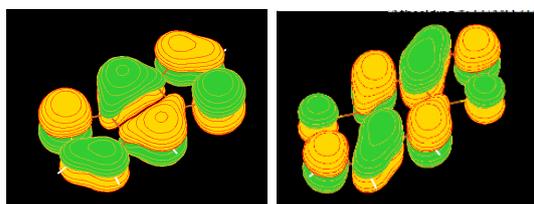


Figure 4: BDT frontier orbitals: (HOMO, LUMO, and LUMO+1)

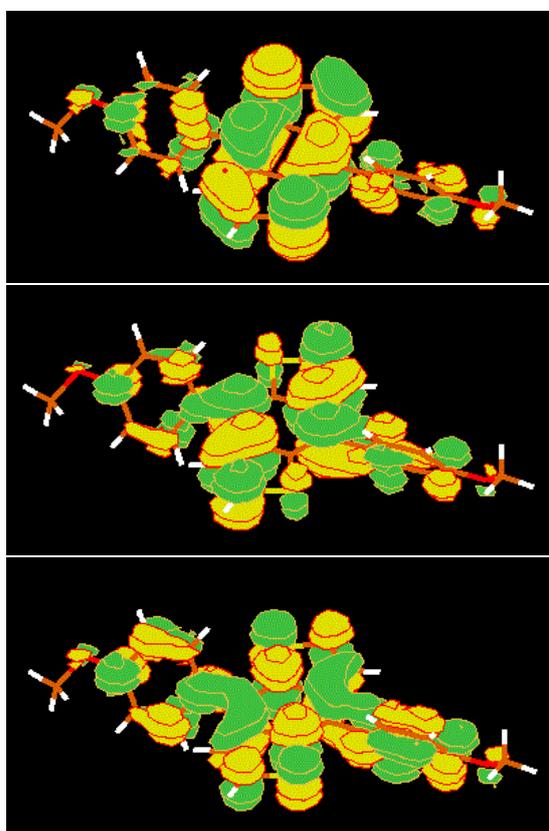
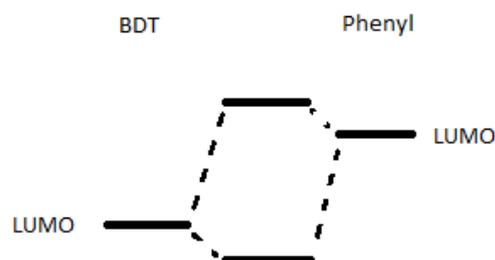


Figure 5: Monomer frontier orbitals: (HOMO, LUMO, and LUMO+1)

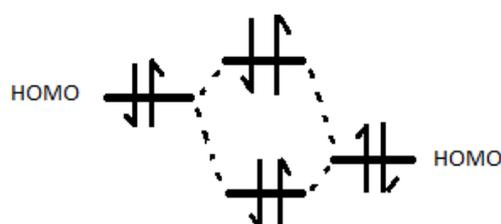


Figure 6: Schematic energy diagram of the monomer

the HOMO-LUMO gap was smaller than that of methoxybenzene because of larger conjugated system, and consequentially it supplied the higher energy level orbital for the anti-bonding combination forming the reference molecules HOMO and the lower energy level unoccupied orbital forming the LUMO, causing the major character of these frontier orbitals to be the BDT HOMO and LUMO. There was a limited spread of these frontier orbitals towards the phenyl groups and as a result, any functional change to the phenyl group would see its influence on the polarizability limited because it would be unable to affect the frontier orbitals situated on the BDT moiety directly.

$$E_2 = \sum_{i \neq 0} \frac{\langle \phi_0 | V | \phi_i \rangle \langle \phi_i | V | \phi_0 \rangle}{E_0 - E_i} \quad (2)$$

From perturbation theory, it is known that the polarizability is the second derivative of the energy to the applied electric field of the sum over all directions and all single orbital excitations divided by the energy gap (formula 2) [17]. A large overlap and a small energy gap would allow for a high contribution to the polarizability. The HOMO, LUMO, and LUMO+1 were all situated on the BDT part and could have interactions to give rise to high polarizability. The energy gaps between the HOMO and LUMO and HOMO and LUMO+1 could be the main criterion for the polarizability.

To improve the polarizability per molecular van der Waals volume using functional changes to the phenyl part of the monomer, multiple strategies were considered. One strategy was to lower the overall energy of the orbitals in the phenyl moiety through electron withdrawing groups, thereby providing a more equal LUMO on this part to the BDT LUMO and thereby allowing the linear combination forming the LUMO of the monomer to take on more of a methoxybenzene character, allowing it to spread more beyond the BDT backbone, and allow for a larger polarizability in its interaction with the BDT-localized HOMO. The other strategy was the opposite, to raise the energy level of the phenyl ring by increasing the density of electrons with electron donating groups, thereby facilitating a better HOMO-HOMO interaction, also increasing the opportunity for better communication between the two parts and reducing the dihedral angle, thereby allowing the HOMO of the molecule to

spread more and allow more interactions with unoccupied molecular orbitals in the molecule, increasing the polarizability that way. Alternatively, extending the  $\pi$ system of what was now the methoxybenzene would allow both strategies to work at the same time as the gap between HOMO and LUMO of this part would be lowered.

## 2.6 Hammett parameters

The empirical Hammett parameter was employed to quantify electron withdrawing and electron donating groups as they were connected to the phenyl part. [18] [19] It could be used to find a relation between the strength of such electron withdrawing and donating effects and the resulting polarizability per molecular van der Waals volume. This would improve the understanding of the monomer and allow for predictions which functional groups could give higher polarizability per molecular van der Waals volume.

The Hammett equation was devised back in the 1930s [20] to create an empirical formula to describe the activating or deactivating nature of electron donating and electron withdrawing functional groups attached to an aromatic ring. A  $\sigma$ parameter was assigned to each functional group depending on the relative position of this group, based on the change in pKa of benzoic acid through the equation:

$$\text{Log} \frac{K}{K_0} = \sigma \rho \quad (3)$$

or through a similar model reaction of which the different sensitivity was modeled through a different  $\rho$ , which then would be related to the change in pKa of functionalized benzoic acid.

The positions for which this Hammett parameter was calculated were the meta and para position to prevent the influence of steric hindrance and other effects through space as opposed to through the aromatic ring. In later times, the standard measured response to a functional group was the chemical shift in NMR spectra [18], in that way measuring the activation of the aromatic system because of the functional group, and these results could then be correlated to the standard values of the Hammett parameter using the  $\text{pK}_a$  of functionalized benzoic acid.

By further analyzing these measured parameters at the para and meta position more detail on the activating or deactivating nature of the functional group can be calculated by separating its contributions into an inductive part and a resonance component. Through further standard reactions, in this case on functionalized bicyclooctane carboxylic acid or quinclidine, both of which are rigid structures of 6 membered carbon rings, but without aromaticity. The  $\text{pK}_a$  of either the acid or the tertiary amine would then be describing the inductive effect of the functional. The difference between this and the Hammett parameter at either the meta or para position would be the resonance contribution of the functional group. These results could be extended over the whole set of measured Hammett parameters using correlated fit for  $\sigma_I$  and  $\sigma_R$  with the measured  $\sigma_m$  and  $\sigma_p$ .

In order to maximize the polarizability of the molecule using functionalities it would be the goal to find a correlation between the activating nature of a functionality and its effect on the calculated polar-

izability of the model, in such a way both providing a direction on how to improve or finding the perfect Hammett parameters a functionality should have, as well as framing the results of these calculations in terms of relative position, resonance, and inductive contributions.

The goal was to discover a molecule related to diphenyl-BDT with a high polarizability per volume, in which particular attention would be given to the HOMO-LUMO gap, the HOMO-LUMO+1 gap, and the dihedral angle between the two aromatic systems, as well as the electronic contributions of the functional groups to understand the approach to improve the polarizability per molecular van der Waals volume.

### 3 THEORY

#### 3.1 Orbital description of polarizability

The interaction of a molecule with a static electric field can be described as a perturbation to the Hamiltonian operator, where  $V$  describes the energy as a consequence of the applied static linear electric field.

$$H = H_0 + \lambda V \quad (4)$$

The wavefunction and the energy of the resulting Schrödinger equation can be written as a Taylor expansion to describe the  $n$ 'th order correction to the wavefunction caused by the perturbation of the electric field.

$$\begin{aligned} (H_0 + \lambda V)(\lambda^0 \Psi_0 + \lambda^1 \Psi_1 + \lambda^2 \Psi_2 + \dots) = \\ (\lambda^0 E_0 + \lambda^1 E_1 + \lambda^2 E_2 + \dots) \\ (\lambda^0 \Psi_0 + \lambda^1 \Psi_1 + \lambda^2 \Psi_2 + \dots) \end{aligned} \quad (5)$$

by pairing up the equations by  $\lambda$  order to ensure the equation in formula 5 holds for all  $\lambda$ , the unperturbed Schrödinger equation, the first correction to the energy, and the second correction to the energy follow.

$$H_0\Psi_0 = E_0\Psi_0 \quad (6)$$

$$H_0\Psi_1 + V\Psi_0 = E_0\Psi_1 + E_1\Psi_0 \quad (7)$$

$$H_0\Psi_2 + V\Psi_1 = E_0\Psi_2 + E_1\Psi_1 + E_2\Psi_0 \quad (8)$$

This relates to the energy and the dipole of a molecule in an electric field:

$$\mu = \mu_0 + \alpha F + \beta F^2 \dots \quad (9)$$

Where  $\mu_0$  is the dipole of the molecule in absence of a field, and where  $\alpha$  is the second derivative of the energy to the field the induced dipole or polarizability. Further terms denote hyperpolarizabilities. This second derivative of the response of the molecule to an applied electric field as in formula 5, is described by formula 8.

The correction to the wavefunction can be expanded in the solutions to the unperturbed Schrödinger equation ( $\Psi_1$  is sum over  $c_i\phi_i$ ), excluding  $c_0$  to preserve orthonormality, which then can be multiplied from the left by  $\phi_0^*$  after which the equation is integrated on both sides. Both the terms with  $\Psi_2$  are describing  $E_0$  and are equal:

$$\begin{aligned} \sum_{i \neq 0} c_i \langle \phi_0 | V | \phi_i \rangle = \\ E_1 \sum_{i \neq 0} c_i \langle \phi_0 | \phi_i \rangle + E_2 \langle \phi_0 | \phi_0 \rangle \end{aligned} \quad (10)$$

The integrals at the energy side of the equation resolve to respectively 0 and 1

because  $i$  can not be 0. The description for  $E_2$  is:

$$E_2 = \sum_{i \neq 0} c_i \langle \phi_0 | V | \phi_i \rangle \quad (11)$$

This energy then depends only on the first correction to the wavefunction  $\psi_1$ . This wavefunction can be found by multiplying formula 7 from the left by a function other than  $\phi_0^*$ ,  $\phi_j^*$

$$\begin{aligned} \sum_i c_i \langle \phi_j | H_0 | \phi_i \rangle + \langle \phi_j | V | \phi_0 \rangle = \\ E_0 \sum_i c_i \langle \phi_j | \phi_i \rangle + E_1 \langle \phi_j | \phi_0 \rangle \end{aligned} \quad (12)$$

Through the orthonormality of the solution of the Hamiltonian the summations give nonzero answers only for the case where  $i=j$ , and the term for  $E_1$  disappears for the same reason:

$$c_j E_j + \langle \phi_j | V | \phi_0 \rangle = c_j E_0 \quad (13)$$

$$c_j = \frac{\langle \phi_j | V | \phi_0 \rangle}{E_0 - E_j} \quad (14)$$

Where  $c_j$  are the coefficients for  $\phi_j$  from which the first correction wavefunction  $\Psi_1$  is built. Entering this in formula 11 gives formula 15, of which the second derivative to the electric field results in the polarizability  $\alpha$ :

$$E_2 = \sum_{i \neq 0} \frac{\langle \phi_0 | V | \phi_i \rangle \langle \phi_i | V | \phi_0 \rangle}{E_0 - E_i} \quad (15)$$

Which shows that the polarizability depends on the interaction integral of the ground state and an excited state, the energy gap between those states, and on the opposite parity of the two states as the perturbation of the electric field was static and linear.

### 3.2 Dielectric Constant relation with polarizability

This polarizability is a molecular property, however, while the dielectric constant that is to be maximized is a material property. The polarizability tensor ( $\alpha$ ) describes the induced dipole ( $\mu$ ) by an electric field ( $F$ ), so to relate this to a dielectric constant the response per volume has to be calculated. The polarization  $P$  is the induced dipole per volume by an applied field [15]:

$$P = \frac{\mu}{V} = \frac{\alpha F_{local}}{V} \quad (16)$$

This causes an electric field in the material in response to the applied electric field and this causes a difference between the applied electric field and the local field, where  $\epsilon_0$  is the vacuum permittivity [15]:

$$F_{applied} = F_{local} + \frac{P}{\epsilon_0} \quad (17)$$

The same difference between external and internal field would also have been described by the permittivity of the material [15].

$$F_{applied} = \epsilon F_{local} \quad (18)$$

The dielectric constant of a material is the permittivity divided by the vacuum permittivity. Introducing formula 16 in formula 17, and then combining formula 17 and 18 allows the relation between dielectric constant and polarizability to be found:

$$\epsilon_r = 1 + \frac{\epsilon_0 \alpha}{V} \quad (19)$$

This polarizability per volume could be defined by modeling the molecule in a crystalline phase, where the volume would be the volume of the unit cell and the polarizability would be calculated per unit

cell. Both the dielectric constant  $\epsilon_r$  and the polarizability  $\alpha$  are tensors, but because of the randomized distribution of the monomer within a polymer chain the direction component was not considered and the average dielectric constant and average polarizability were calculated.

## 4 Method

Geometry optimization of the series of potential monomers was done with DFT calculations using the Gamess-UK package [21] with B3LYP functionals and with a 6-31G\*\* basis set. To reduce calculation times the triethylene glycol chains were modeled as methoxy groups given that the polarizability was calculated in the time frame where only electronic effects would contribute and further lengths of the TEG chain would not extend the aromatic  $\pi$ -system as the carbon in the TEG chain with  $sp^3$  hybridization would have no electrons to participate with.

The polarizability calculations using these optimized geometries were performed with DFT calculations using the Dalton package [22], the polarizability calculated using the coupled perturbed Kohn Sham (CPKS) method [23] with the aug-cc-pVTZ basis set.

The XRD sourced crystal structure of the reference molecule, as well as the dinitrothyl analog, were optimized with DFT calculations using the CRYSTAL14 package [24], with B3LYP functionals and a 6-31G\* basis set using a 2x2x2 k-point mesh. Both the geometry and the lattice parameters were optimized. Grimme dispersion correction [25] was employed for

Atomtype	C <sub>6</sub> (Jnm <sup>6</sup> mol <sup>-1</sup> )	Van der Waals Radius (Å)
H	0.14	1.001
C	1.75	1.452
N	1.23	1.397
O	0.70	1.342
F	0.75	1.287
Cl	5.07	1.639
P	7.84	1.705
S	5.57	1.683

Table 1: Grimme dispersion parameters

these optimization calculations with individual parameters for every atom type as per Table 1. Further functional groups with relatively small changes to the molecular structure were introduced to find model crystal structures for these alternative monomers. At the same level of calculation, dielectric constants of these molecules were calculated using the CPKS method as implemented in CRYSTAL14 [26].

Molecular van der Waals volumes were calculated by associating a van der Waals radius as per Table 2 to each atom type [27], after which the molecule was placed in a 0.05Å grid, each grid point associated with a 0.125mÅ volume. This multiplied by the number of grid points within the van der Waals radius of one of the atoms of the molecule gives the molecular van der Waals volume. [28]

Atomtype	Van der Waals Radius (Å)
H	1.20
C	1.70
N	1.55
O	1.52
F	1.47
Cl	1.75
P	1.80
S	1.80

Table 2: van der Waals radii

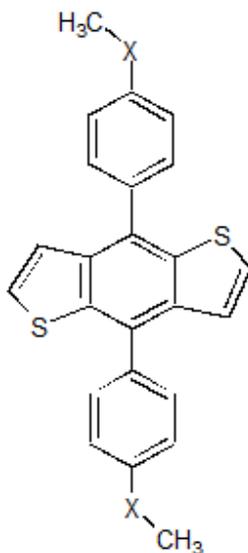


Figure 7: Monomer with change at X position (para)

Molecule (X)	Polarizability (Å <sup>3</sup> )	Polarizability per van der Waals volume
Base (H)	2470	7.096
Phosphoryl	3059	6.620
Ester	2744	6.983
Phosphine	3131	6.866
N(CH <sub>3</sub> )	2841	7.228

Table 3: polarizability results

## 5 Results

### 5.1 Polarizability calculations

A set of molecules with different functional groups was calculated, mostly with changes at the para and meta position. The TEG chain was required to improve solubility during solar cell manufacturing and improved the nuclear contribution to the dielectric constant. [11] Changes to the para position then involved groups that could connect to such a TEG chain. To extend the options, further tests were executed with the TEG chain at the meta position to allow for different functional groups at the para position.

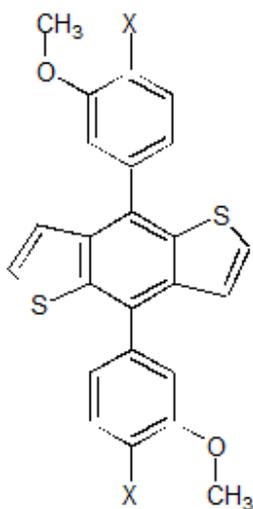


Figure 8: Alternative monomer with change at X position (para)

Molecule	Polarizability ( $\text{\AA}^3$ )	Polarizability per van der Waals volume
H	2424	6.966
OH	2518	6.917
NH <sub>2</sub>	2650	7.162
CH <sub>3</sub>	2633	6.911

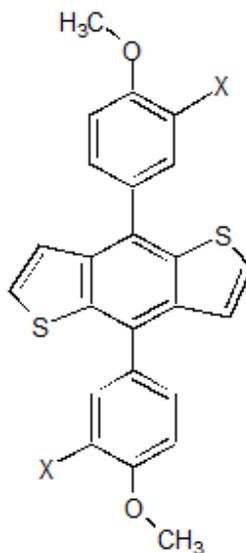


Figure 9: Monomer with change at X position (para)

Molecule	Polarizability ( $\text{\AA}^3$ )	Polarizability per van der Waals volume
Base (H)	2470	7.096
F	2479	6.924
Cl	2657	7.048
CF <sub>3</sub>	2670	6.527
OH	2544	6.989
NO <sub>2</sub>	2750	6.980
CN	2739	7.170

Only the result for the primary amine and the TEG chain connected at the meta position is higher than the reference monomer. The polarizability is increased significantly by phosphine or a tertiary amine connecting to a TEG chain, but these options increase the polarizability while increasing the volume of the molecule. Electron withdrawing groups have worse results in polarizability per molecular van der Waals volume in both series, so the electron donating ether of the TEG chain in reference molecule is already a good option.

At the meta position, only the cyanide functional group improved the polarizabil-

Molecule	Polarizability ( $\text{\AA}^3$ )	Polarizability per van der Waals volume
(o,m)Cl <sub>2</sub>	2799	6.828
(m,p)F <sub>2</sub>	2417	6.587
Naphthyl	3401	7.801
Naphthyl-CN	3065	7.402
Amine-Ester	2809	7.130

ity per molecular van der Waals volume. Apart from the trifluoromethyl functional group, small differences were achieved compared to the reference in polarizability per molecular van der Waals volume, and relatively small differences are also found in the polarizabilities calculated. The bigger factor appears to be the molecular volume which is increased by the alternative functional groups, with three electron withdrawing groups giving the worst polarizability per van der Waals volume: the trifluoromethyl, cyanide and nitro group. All of the groups tested here except the trifluoromethyl extend the  $\pi$ -system, either by donating lone pairs or accepting  $\pi$ -electrons. It can then be understood that the volume increase of the molecule by trifluoromethyl does not proportionally increase the polarizability as it does for the other functional groups.

The final molecules tested were those with multiple changes, as well as with asymmetric functional groups. Di-difluorophenyl-BDT had made only a minor change in polarizability compared to the reference and it can be understood that both the oxygen of the TEG chain and the fluorine it replaced it in this alternative were inductively electron withdrawing and donating to the aromatic ring through their lone pair electrons, albeit at different rates. The molecule di-dichlorophenyl-BTD saw a comparable reduction in polarizability per molecular van der Waals volume as the one chlorine had done compared to the reference

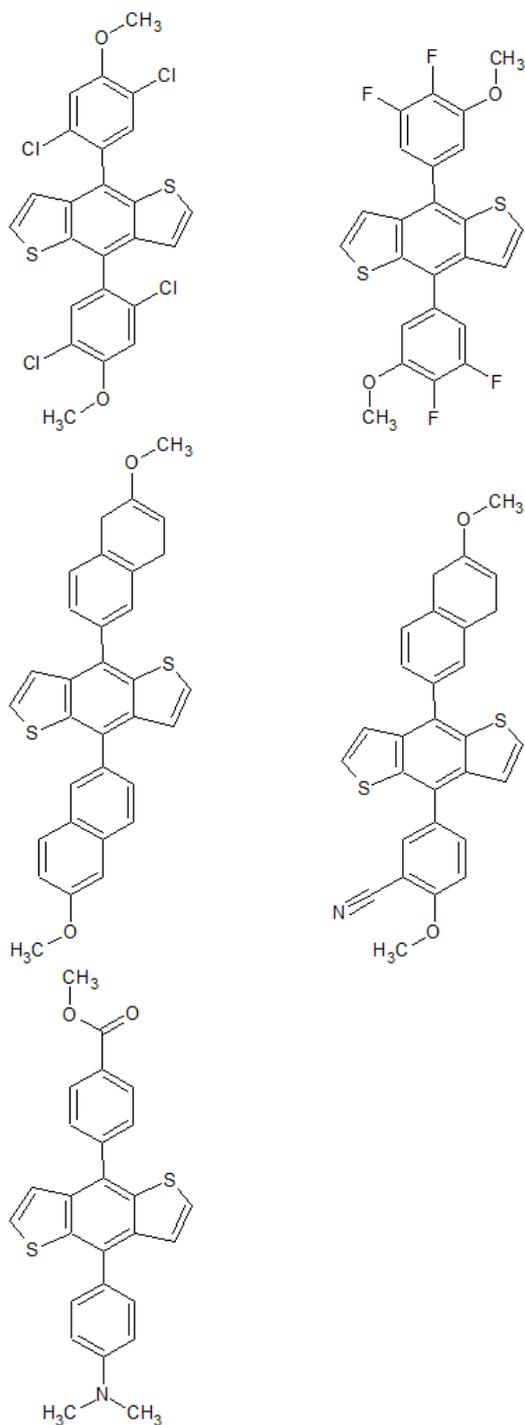


Figure 10: Alternative monomers; symmetric and asymmetric

monomer.

The highest polarizability per molecular van der Waals volume was found for the molecule where the phenyl was replaced by a naphthyl group. This extension of the  $\pi$ -system would be understood to have high polarizability in isolation but was also thought to allow this aromatic system to have energy levels that matched better to the energy levels of the more extended  $\pi$ -system of the BDT backbone.

Where symmetric molecules were the first focus because of the relative ease of synthesis, an investigation was also made into two asymmetrically functionalized molecules with a push-pull philosophy, in which it was found that the results very close to the average of both symmetrical polarizability values with these functional groups. This can be rationalized through the limited communication between the aromatic systems. This strategy to set up an electron density gradient across the molecule which could disproportionally affect the LUMO increasing the polarizability cannot make this change through the bond connecting the phenyl to the BDT unit. There is no significant benefit to an asymmetric strategy of functional groups.

## 5.2 Relation with molecular properties

The dihedral angle of the bond between the phenyl and the BDT part was changed only slightly by functional groups at the para and meta position. With a functional change at the ortho position as with molecule di-dichlorophenyl-BTD, a large change is observed from around 60 degrees to above 75 degrees. This is due to steric

hindrance. This steric hindrance would prevent improvement of the spread of the aromatic systems through this bond and impede the progress a functional group could make at improving the polarizability per molecular van der Waals volume. No other functional groups were considered at the ortho position to the BDT for this reason.

There is a relation between the dihedral angle between the phenyl and BDT part and the polarizability per molecular van der Waals volume when the sterically hindered outlier of molecule di-dichlorophenyl-BTD is removed from the results. Curious is the example of the large difference between the cyanide and nitro groups, which are both strong resonance electron withdrawing groups, which have comparable polarizabilities per van der Waals volume but have very different dihedral angles between the two aromatic systems. Electron donating groups and extensions of the  $\pi$ -systems at the para position caused a smaller dihedral angle suggesting a better interaction between the phenyl group and the BDT part.

There is no convincing correlation between the HOMO-LUMO gap and the polarizability per molecular van der Waals volume, and similarly, there is no relationship between the HOMO-LUMO+1 gap and the polarizability per van der Waals volume. The close results around the 4.05 eV gap for the HOMO-LUMO gap and the 4.7 eV gap for the HOMO-LUMO+1 gap will lower the standard deviation of any fit attempt on this data. The outlier of the naphthyl group seems to be the main cause of the negative gradient that would be expected for the relation between the

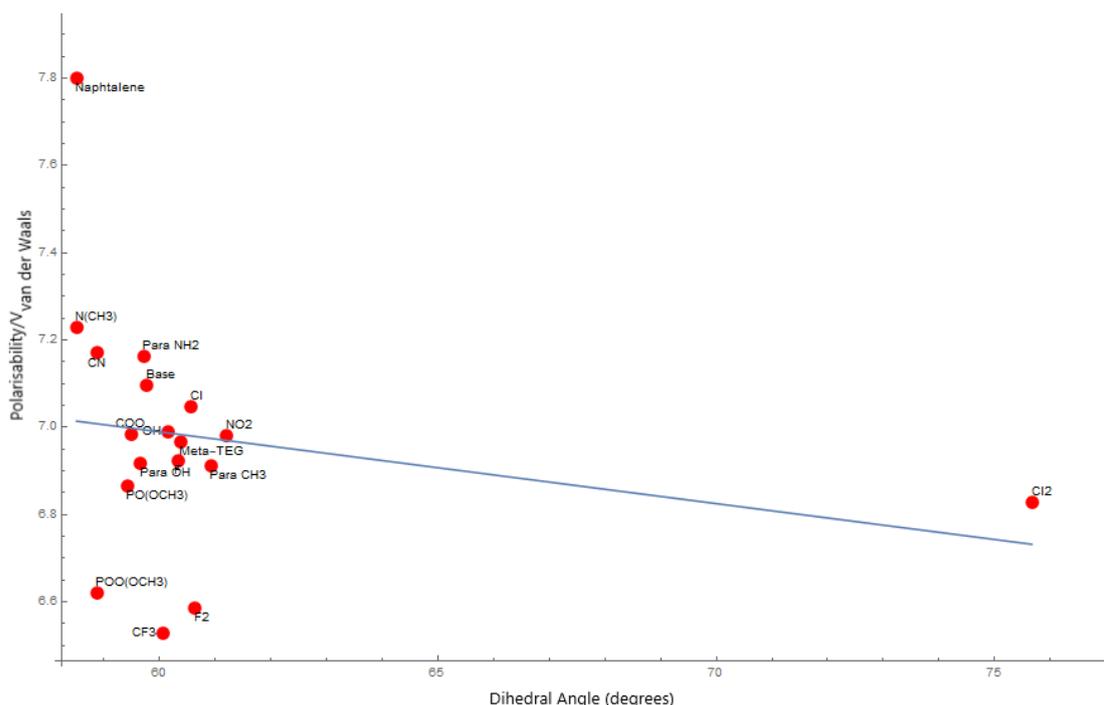


Figure 11: Relation polarizability and dihedral angle (STD:0.276)

polarizability and the energy gaps. The highest energy gaps are those of the sterically hindered molecule di-dichlorophenyl BDT 4.21 eV and 4.89 eV.

The energy gaps for molecules with changes to the functional group at the meta position were relatively unchanged. For the reference monomer, the contribution of the frontier orbitals at the meta position was low and a functional group at that position could affect the overall electron density of the phenyl part, but would not affect the frontier orbitals. The LUMO+1 had a larger contribution at the meta position and for strong resonance electron withdrawing groups as nitro and cyanide groups, the LUMO+1 was lowered in energy to the point where it became the LUMO of those monomers. This did not

improve the polarizability per molecular van der Waals volume.

Changes to the functional group at the para position did modify the HOMO-LUMO gap, and also previously showed a larger spread in dihedral angles depending on the functional group. The contribution of the frontier orbitals to the para position was larger, though not equal, and as such it can be understood that the para position modifies both the HOMO-LUMO gap as well as modifying the ability of the phenyl part to interact more favorably with the aromatic system of the BDT part and reducing the dihedral angle. Electron withdrawing groups at the para position reduced the HOMO-LUMO gap suggesting the contribution of the LUMO at the para position was larger than that of the HOMO.

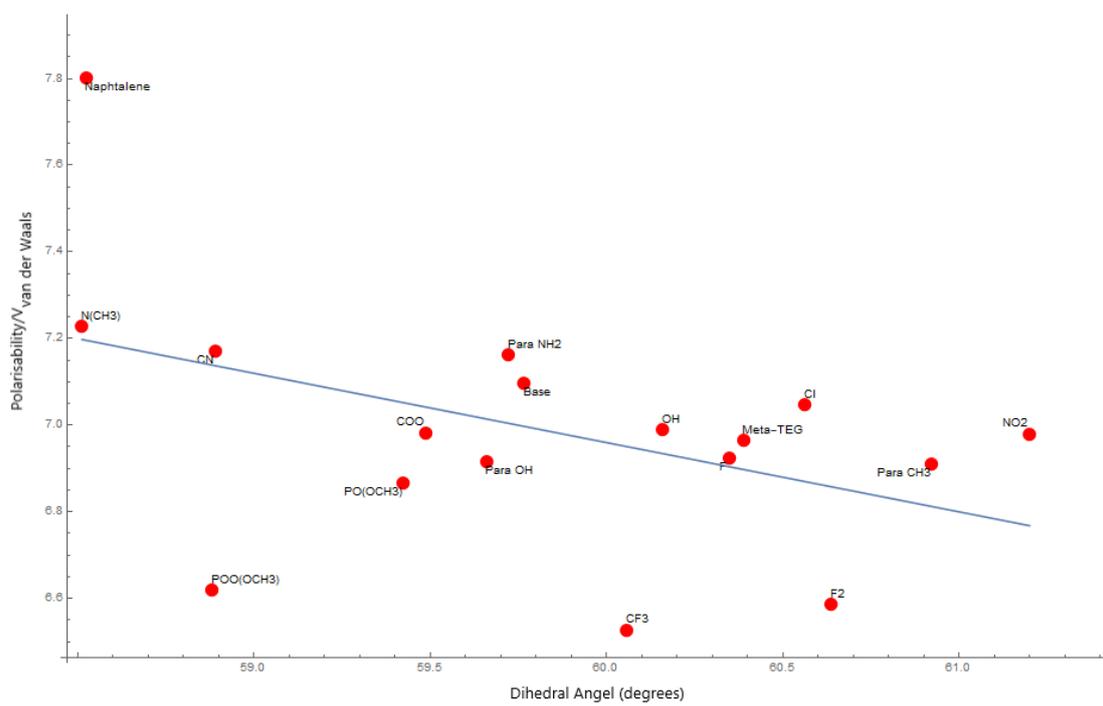


Figure 12: Relation polarizability and dihedral angle without steric hindrance (STD: 0.258)

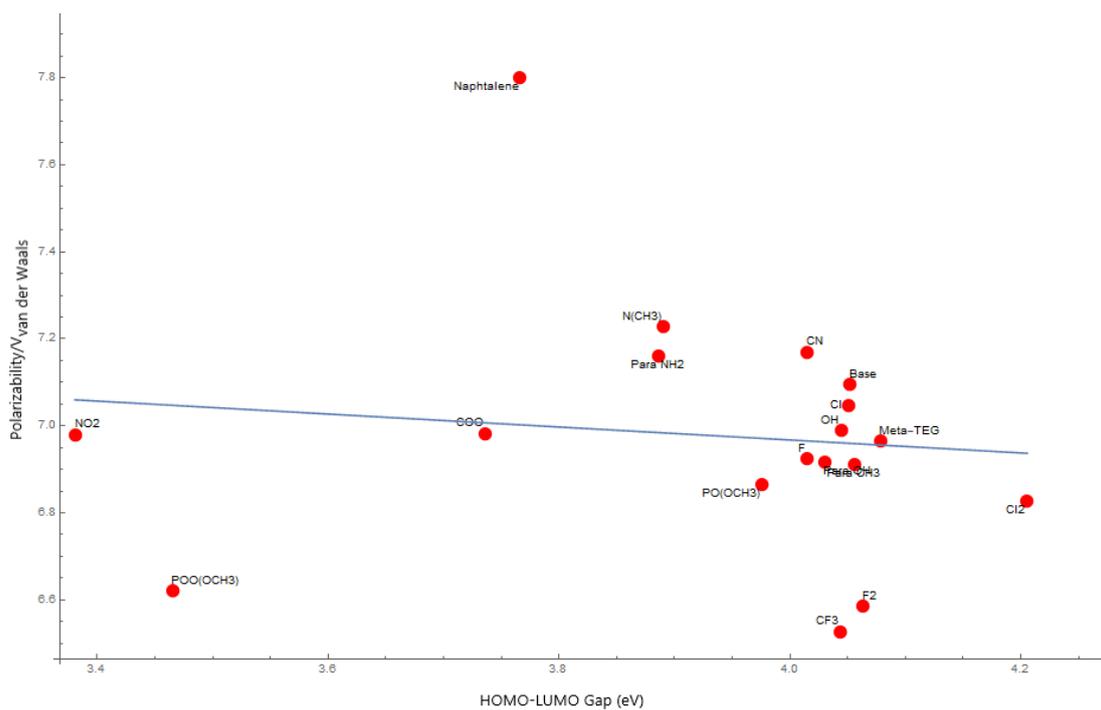


Figure 13: Relation polarizability and HOMO-LUMO gap (STD:0.281)

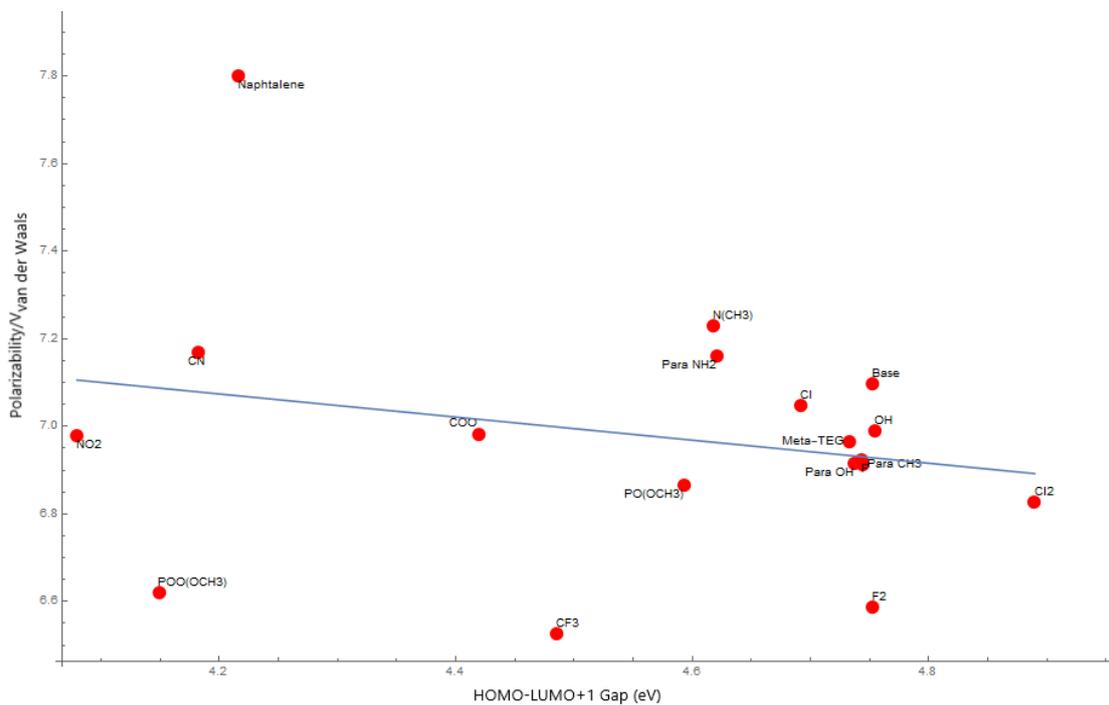


Figure 14: Relation polarizability and HOMO-LUMO+1 gap (STD:0.275)

From the results of the dihedral angle and the HOMO-LUMO and HOMO-LUMO+1 gap, functional changes at the para position showed the largest ability to change the behaviour of the molecule.

### 5.3 Relation with Hammett parameters

The next step was to quantify these observations about electron donating or electron withdrawing groups using the Hammett parameters and to provide a relation in which they could be predictive of polarizabilities per molecular van der Waals volume. At the para position this would be for two different reference molecules, so two different baselines, but it would be expected that the relationship to the parameter of the functional group at the para position was similar, so a linear fit of those was constructed where the gradient was a weighted average of both, while their offsets were different.

At the para position, the best fit for the polarizability per molecular van der Waals volume results was the  $\sigma_p$  Hammett parameter with a standard deviation: 0.220. The change in polarizability per molecular van der Waals volume of the monomer can be described in terms of phenyl ring activation and deactivation. Electron donating effects would improve the polarizability per molecular van der Waals volume.

The aromatic properties of naphthyl could also be related to the phenyl ring as a functional group with a Hammett parameter. However, as the naphthyl is the main outlier, this approach undervalues the contribution of the additional connected aro-

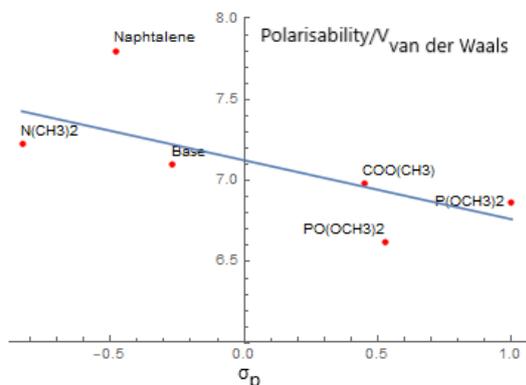


Figure 15: Relation polarizability para-Hammett parameter (weighted average fit) (STD:0.220)

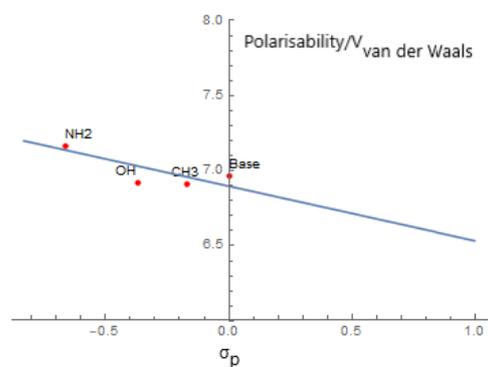


Figure 16: Relation polarizability para-Hammett parameter for alternative monomer (weighted average fit) (STD:0.220)

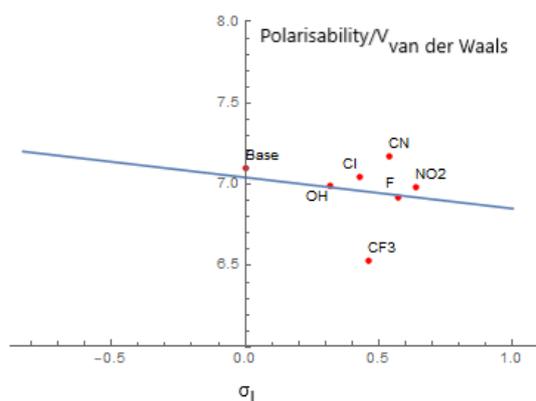


Figure 17: Relation polarizability inductive-Hammett parameter (STD:0.204)

matic ring for the purposes of this molecule. This could be an extension of the aromatic system compares favorably for the polarizability compared to functional groups which donate or withdraw  $\pi$ -electrons, or because the Hammett parameter is only capable of describing activation and deactivation where an extension of the aromaticity also lowers the energy gap of that part.

Electron donating groups improve the polarizability per molecular van der Waals volume. Other than the strategy to extend the aromatic systems, the strategy to increase the electron density of the phenyl part to match it better to the energy levels of the BDT part appears to be a legitimate strategy.

With the TEG chain at the meta position the offset for the fit lowered, and the primary amine is the sole functional group that improves the polarizability per molecular van der Waals volume of the reference molecule. The ether of the reference molecule is a strong electron donating functional group with a small van

der Waals volume, there are few options which are able to improve the reference molecule.

## 5.4 Relation with dielectric constant

The polarizability per volume change for functional groups at the meta position correlated well with the  $\sigma_I$  parameter (standard deviation: 0.204) as well with the  $\sigma_m$  parameter (0.207). This was further confirmation that the frontier orbitals are relatively untouched by the functional groups at the meta position as the correlation with the inductive contribution alone was a better predictor of the resulting polarizability per molecular volume as the combination of inductive and resonant contributions.

The gradient of -0.19 is significantly smaller than the gradient of the fit for the functional changes at the para position (0.36). This can also be understood in that both the HOMO and the LUMO of the reference molecule have small contributions to the meta position. The LUMO+1 is affected by a resonance electron donating or withdrawing group, and for the cyanide and the nitro functional groups, this was lowered in energy to the extent that this became the LUMO of these functionally changed monomers. This does not appear to be the cause of the highest polarizability per molecular van der Waals volume of the cyanide functional group, contrary to the overall trend where also on the meta position electron donating groups are performing better. The nitro functional group would have been expected to perform better than as it had the lower HOMO-LUMO gap, and a comparable resonant electron

withdrawing ability.

A possible explanation for the higher result of the cyanide functional group could lie in the 180 degree bond angle, placing the extension of the  $\pi$ -system further away from the axis of the molecule, which would allow the electric field induced dipole to be larger, while compared to a nitro functional group a cyanide group is less voluminous.

The other outlier is again the trifluoromethyl which performed worse than would be expected from this relation. It was not expected that the focus on just the inductive contribution stood out, as the same outlier was present in the fit with  $\sigma_m$ . The cause of this outlier has to be found in the correction with the molecular van der Waals volume where for the other functional groups at the meta position this increased volume also participates in the  $\pi$ -system of the phenyl group. The voluminous trifluoromethyl cannot participate through the  $sp^3$  hybridized carbon. There is a smaller advantage in polarizability associated with the volume compared to other functional groups tested at the meta position.

Inductively donating groups which would extend the  $\pi$ -system were then expected to give improved polarizability per molecular van der Waals volume results, but smaller improvements would be expected compared to changes in the functional group at the para position and the volume associated with the functional group would consequently be a relatively larger factor at the meta position.

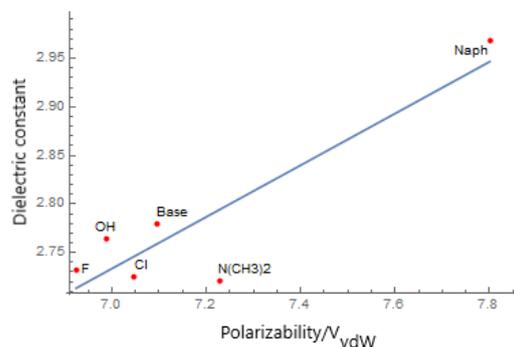


Figure 18: Relation dielectric constant with polarizability per molecular van der Waals volume (STD:0.041)

Polarizability per van der Waals volume is a good predictor of the dielectric constant, and the relation confirms that the best option to improve the polarizability of this monomer is by extending the  $\pi$  system. With only the electrical component of the dielectric constant considered, a value of 2.97 was calculated for dinaphthylbenzodithiophene with triethyl glycol chains.

The reference molecule was a good option for a diphenyl-BDT with a high optical dielectric constant. The monomer with a tertiary amine connecting the ethylglycol chain was predicted to improve the dielectric constant based on the polarizability per molecular van der Waals volume but had a significantly lower dielectric constant. Within a crystal structure resembling the crystal structure of the reference monomer, the more voluminous tertiary amine caused a disproportionate increase in the unit cell size. The shape of the molecule is also a factor in a crystal, to allow molecules to stack in an efficient manner and the molecular van der Waals volume does not account for this.

## 6 Conclusion

Dielectric constants were calculated using a model for diphenyl-benzodithiophene with attached triethyl glycol chains which were calculated with DFT with B3LYP functionals and a 6-31G\* basis set. At the para and the meta position from the benzodithiophene on the phenyl of this model, changes were made to the functional group to improve the dielectric constant, which would improve the characteristics for solar cell performance. A good relationship was found between the dielectric constant and the molecular polarizability divided by the molecular van der Waals radius. Polarizabilities were calculated with DFT with B3LYP functionals and an aug-cc-pVTZ basis set for molecules which geometry was optimized using DFT with B3LYP functionals with a 6-31g\*\* basis set.

A relation was found between the dielectric constant and the polarizability per molecular van der Waals volume. To improve the dielectric constant and the polarizability per molecular van der Waals volume, two relationships were found. Electron donating functional groups were beneficial for the polarizability per molecular van der Waals volume at the para position from the BDT. Only the cyanide functional group improved the polarizability per molecular van der Waals volume at the meta position, but otherwise, inductively electron donating groups would perform better. The functional group changes were nearly twice as effective at the para position compared to the meta position.

Steric hindrance was observed for chlorine at the ortho position. A relationship was found where a smaller dihedral angle

between the BDT and the phenyl parts of the monomer related to a larger polarizability per molecular van der Waals volume. There was no clear relation between the HOMO-LUMO gap or the HOMO-LUMO+1 gap and polarizability per molecular van der Waals volume.

The highest optical dielectric constant was achieved by extending the pi system to dinaphthyl-benzodithiophene with triethyl glycol chains, with an optical dielectric constant of 2.97, an improvement over diphenyl-benzodithiophene with triethyl glycol chains with an optical dielectric constant of 2.78

For future investigation in this monomer, crystal structures and volumes of monomers with changes at the para position should be considered to further solidify the relationship between polarizability divided by van der Waals volume and the dielectric constant. For alternative options to improve the dielectric constant extended electron-rich aromatic systems should be considered as side groups to benzodithiophene.

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