

Optical absorption in donor–acceptor polymers – alternating vs. random†

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We investigate in a combined theoretical and experimental study the influence that the specific arrangement, e.g., alternating or random, of donor and acceptor units has on the optical absorption of extended molecules. Because of its important role in low gap polymers we discuss in particular the energetic position of the first electronic transition. We theoretically determine the excitations in extended oligomers with thiophene as the donor and 2,1,3-benzothiadiazole as the acceptor component by using time-dependent density functional theory based on non-empirically tuned range separated hybrid functionals. Corresponding systems are synthesized and theoretical and experimental data are critically compared to each other. We conclude that the influence of the specific arrangement of donor and acceptor monomers on the optical gap is limited and that effects beyond the single molecule level effectively limit the size of the experimentally observed optical gap.

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1 Introduction

The search for low gap polymers is an important step in improving the efficiency of organic solar cells based on conjugated polymers.^{1–5} For systematically designing low gap polymers it is beneficial to understand the complex electronic processes that typically occur in these systems. The absorption of light that results in an excitation (“exciton formation”) is one important step in the sequence of processes that determine solar cell efficiency.⁶ There are different strategies for obtaining low gap polymers.⁴ Among the most important ones are increasing the conjugation length, e.g., by increasing the planarity of the polymer, and the combination of electron rich (donor) and electron poor (acceptor) monomers along the conjugated polymer backbone.⁷ In the latter case the reduction of the bond length alternation and the formation of partial intramolecular charge transfer (CT) excitations between the donor (D) and acceptor (A) moieties are considered to be responsible for the low gap.^{4,8}

In this article we focus on donor acceptor (DA) polymers and analyze how far the specific arrangement of D and A units within a polymer influences the optical absorption. Specifically we address

the question of whether the optical gap and other absorption peaks differ considerably between a molecule with a random arrangement of D and A units and a molecule in which the same total number of D and A units is arranged in a strictly alternating way. The answer to this question is important for our fundamental understanding of DA systems and for developing future synthesis strategies. Usually low gap polymers based on D and A moieties are synthesized by arranging the D and A units in a strict alternating order. Whether this strict alternating order is necessary for lowering the gap is not studied. If this is not necessary and the D and A units can be arranged in any random order to obtain the same effect, then the synthetic strategy to obtain a variety of new low gap polymers can be more innovative involving different kinds of monomers in any random fashion. This also allows improving the solubility of such polymers. Therefore, the question of the importance of the ordering of the D and A units is discussed in this paper.

Our study is based on thiophene (T) as the D and 2,1,3-benzothiadiazole (B) as the A component. Both of these constituents are frequently used in the field of low gap oligomers and polymers for organic photovoltaic devices.^{9–15} We computationally analyze the low lying excitations of these systems in detail. In agreement with other studies of similar systems¹⁶ we find that they can be described as having, at best, “partial” CT character, and we compare the theoretical findings in detail to experiments.

The type of accurate, non-empirical calculations for systems of considerable size that we present here are made possible by

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recent progress in the development of (Time Dependent) Density Functional Theory ((TD) DFT).^{17–24} Specifically, we employ a range separated hybrid (RSH) functional in which the range separation parameter is chosen according to a non-empirical, self-consistent procedure designed to yield a reliable description of excitations in multichromophoric systems.^{21,25,26}

Using the correct functional class to account for the complexity of the excitations in DA polymers is a decisive prerequisite for the type of computational study that we present here.

Our manuscript is organized as follows. In Section 2 we give a brief overview of the studied systems, followed by an outline of the theoretical approach and the experimental synthesis in Section 3. We present the results of our calculations in Section 4, comparing different D–A arrangements and oligomer sizes in a single molecule approach and predicting the effective saturated conjugation length. In the same section we compare the theoretical findings to the corresponding experimental data. Occuring differences are analyzed in Section 5. The maximum achievable conjugation length emerges as the main factor limiting the optical gap.

2 Systems

Fig. 1 and 2 schematically depict the oligomers that we examine in this article. a-BTT and a-BTT-H show strictly alternating arrangements of thiophene (T) as a donor and 2,1,3-benzothiadiazole (B) as an acceptor (upper left and left in Fig. 1 and 2, respectively). The difference between these two systems is the presence of hexyl side chains (H) on the thiophene units in a-BTT-H. The systems r-BTT and r-BTT-H (upper right and right in Fig. 1 and 2, respectively) are molecules in which T and B units are combined to yield random arrangements of T and BT (Fig. 3) components. For a-BTT and r-BTT we did calculations with the number n of repeat units ranging from $n = 1$ to $n = 12$. For illustration we show the optimized structures for the largest

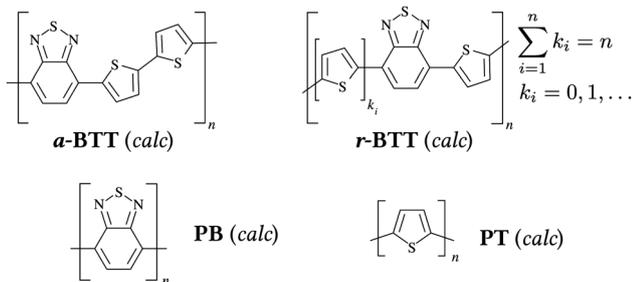


Fig. 1 Schematic of the oligomeric systems examined in the calculations.

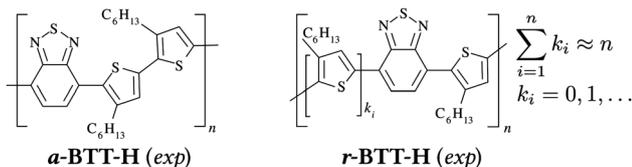


Fig. 2 Schematic of the oligomeric systems examined in experiments. The chain length n can only be determined on average (\bar{n}) from gel permeation chromatography.

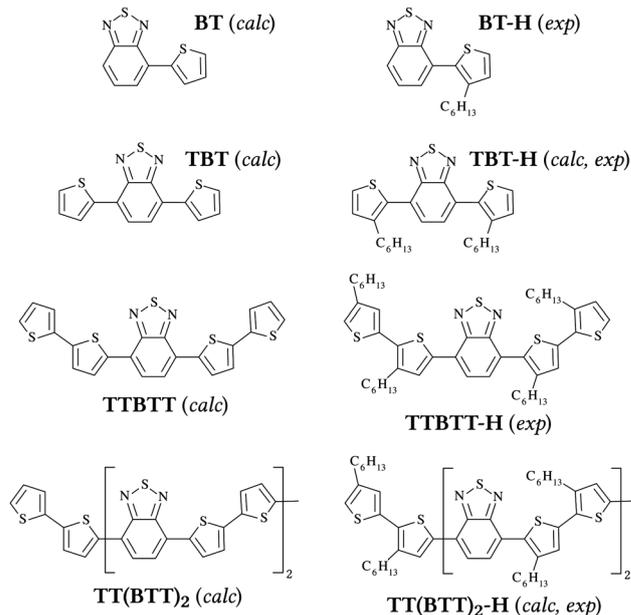


Fig. 3 Schematic of the well defined monodisperse low molecular weight systems examined in experiments (labeled with exp) and calculations (labeled with calc).

oligomeric calculated systems ($n = 12$) in Fig. 4. For reasons that become clear further below it is sufficient to study just one representative for r-BTT, *i.e.*, one specific random arrangement, for each chain length.

In our experiments we synthesized a-BTT-H with an average number \bar{n} of repeat units of $\bar{n} = 4$ and $\bar{n} = 15$ and a polydispersity $M_w/M_n = 1.7$ and 1.6 , as well as r-BTT-H with $\bar{n} = 5$ and $\bar{n} = 10$ and $M_w/M_n = 1.5$ and 1.6 (see caption of Fig. 2). The only difference to the systems that we use in the calculations are the hexyl side chains. The influence of such side chains is discussed in detail in Section 5.

It is important to note that in the calculations we always combined n B with $2n$ T. In this way we ensure that our results are only influenced by the DA arrangement (and not by different D and A ratios). In the synthesis, however, we were only able to obey this rule approximately in the case of r-BTT-H. For a deeper understanding of DA systems and the differences between calculations and experiment we furthermore investigated the donor-only oligomer PT, the acceptor-only oligomer PB as well as the donor–acceptor systems BT, TBT, TBT-H, TTBT, TTBT-H, TT(BTT)₂, and TT(BTT)₂-H as shown in Fig. 3 (monodisperse low molecular weight in experiment).

3 Methodology and synthesis

3.1 Methodology (theory)

The largest systems that we examined in our calculations are conjugated molecular chains with up to 36 aromatic rings. Our method of choice for systems of such size is DFT^{27,28} or TDDFT,^{29,30} respectively, because of its favorable ratio of reasonable quality of results to moderate computational cost. With appropriately chosen functionals, it also allows for little or no empiricism.

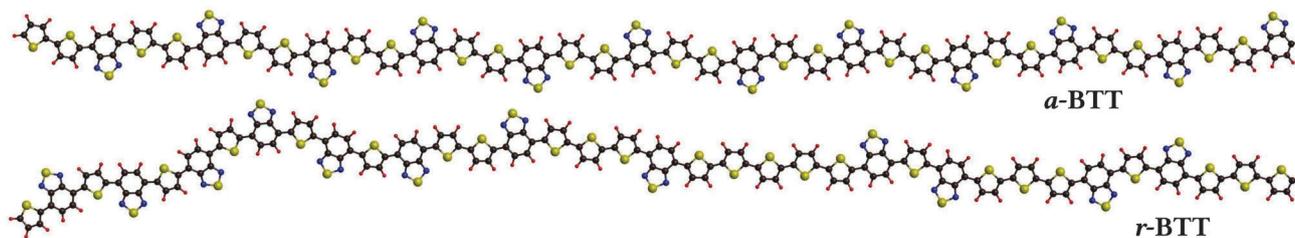


Fig. 4 Optimized geometries of a-BTT and r-BTT for $n = 12$, corresponding to a length of 15 nm. The optimization method is described in Section 3.

We optimized the geometries of the systems in Fig. 1 and 3 using the B3LYP functional³¹ with the def2-SV(P) basis set and the Grimme dispersion correction³² in Turbomole.^{33,34} This choice is pragmatically motivated by previous experience showing that this approach yields reliable geometries for this type of system.

For the calculation of the excitation energies, which is the critical step in our study, we used linear response TDDFT with the Baer-Neuhauser-Livshits (BNL) RSH functional. It combines LDA-type short range exchange and long range Fock exchange with the Lee-Yang-Parr correlation functional.³⁵⁻³⁷ Since we are calculating optical excitation energies we choose the least square gap tuning condition^{26,38}

$$T_{\text{LS}}(\gamma) = \sqrt{\sum_{i=N}^{N+1} [e_{\text{HOMO}}^{\gamma}(i) + E^{\gamma}(i-1) - E^{\gamma}(i)]^2} = \min \quad (1)$$

to determine the range separation parameter γ , which corresponds to approximately twice the inverse of the separation length between short range and long range electronic exchange.^{39,40} $E^{\gamma}(i)$ is the γ -dependent total energy for a system with i electrons and $e_{\text{HOMO}}^{\gamma}(i)$ the eigenvalue of the highest occupied generalized Kohn-Sham orbital. To account for the system specific magnitude of the highest occupied and lowest unoccupied orbitals we performed the tuning for each molecule separately. With the optimized γ we calculate the BNL excitation energies with the program package QChem⁴¹ and the 6-31G(d,p) basis set. We expect reliable results from this procedure because it has been shown, *e.g.* in ref. 16 and 25, that tuned RSH functionals can successfully be applied to DA systems that are similar to the ones studied here, and the resulting excitation energies are consistent with experimental absorption spectra.

In order to test the reliability of this approach we performed several control calculations. To check basis set limitations we optimized the geometries of BT, TBT, and TT(BTT)₂ also with the def2-TZVP basis set (in Turbomole) and performed the γ -tuning and the calculation of the BNL excitation energies with the 6-311G(d,p) basis set (in QChem). In comparison to the calculations with the basis sets mentioned in the previous paragraph, this lead to differences of less than 0.1 eV in the lowest excitation energy. As another test we checked how much using a different RSH functional alters the results. We used the ω PBE functional¹⁸ for the γ optimization as well as the TDDFT calculation on TT(BTT)₂. Compared to the BNL functional the lowest excitation energy changed by only about 0.02 eV. This is

in line with other studies showing that differences between various RSH approaches appear in the ground state energy³⁸ and not in optical and fundamental gaps.^{16,42} Finally, we tested how far environmental influences as described by the COSMO solvation model⁴³ within Turbomole affect the B3LYP geometries and TDDFT excitation energies and found an overall effect of only 0.04 eV.⁴⁴ These tests confirm the validity of our theoretical setup since all the discrepancies are within the limits of the predictive power of our method itself.

3.2 Synthesis and characterization

3.2.1 Monomer synthesis. The synthesis procedures of the monomers M1 and M2 are outlined in Fig. 5. The AB-type monomer M1 is not documented in the literature; the details of the synthesis are given in the ESI.† M1 was obtained by the Ir-catalyzed (Ir(COD)Cl₂) borylation of an asymmetrically substituted compound **1** in the presence of 4,4'-di-tert-butyl bipyridine (dtbpy). The other AB-type monomer M2 is known in the literature but we synthesized it starting from 2-bromo-3-hexylthiophene **2** with the Knochel-Hauser-base (2,2,6,6-tetramethylpiperidinylmagnesium chloride lithium chloride: TMPMgCl-LiCl). Details are given in the ESI.† M3 was synthesized by bromination of 3,4'-dihexyl-2,2'-bithiophene with *N*-bromosuccinimide according to published procedures.⁴⁵ M4 is commercially available.

3.2.2 Polymer synthesis. Following the synthetic route shown in Fig. 6, the AB-type monomers M1 and M2 were used to obtain the conjugated copolymers r-BTT-H ($\bar{n} = 4; 15$). Using monomers M3 and M4 the alternating copolymers a-BTT-H ($\bar{n} = 5; 10$) were obtained. All copolymers were synthesized *via* palladium catalyzed Suzuki coupling polycondensation. A variation of reaction conditions led to different molecular weights for r-BTT-H and a-BTT-H. For synthetic details and characterization see the ESI.†

All four conjugated copolymers are completely soluble in common organic solvents like toluene, tetrahydrofuran or

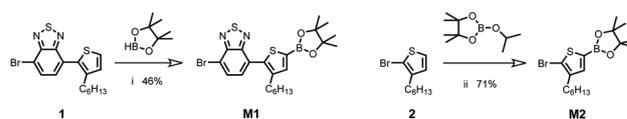


Fig. 5 Synthesis of monomers M1 and M2. Reaction conditions: (i) Ir(COD)Cl₂/dtbpy in tetrahydrofuran at reflux; (ii) TMPMgCl-LiCl in tetrahydrofuran at room temperature.

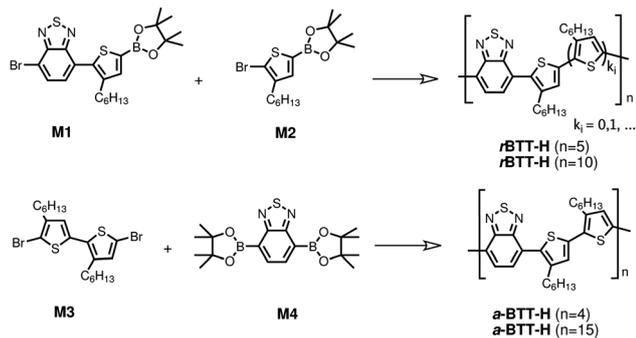


Fig. 6 Synthesis of copolymers r-BTT-H and a-BTT-H.

Table 1 Number average molecular weights (M_n) determined with GPC, polydispersity index (M_w/M_n) and absorption maximum (E_{\max}) of the synthesized compounds

	M_n [g mol ⁻¹] (GPC)	M_w/M_n (GPC)	E_{\max} [eV]
TBT-H			3.08
TTBTT-H	913	1.01	2.46
TT(BTT) ₂ -H	1443	1.04	2.41
a-BTT-H ($\bar{n} = 4$)	1841	1.74	2.38
a-BTT-H ($\bar{n} = 15$)	7201	1.64	2.36
r-BTT-H ($\bar{n} = 5$)	2490	1.46	2.49
r-BTT-H ($\bar{n} = 10$)	4478	1.59	2.45

methylene chloride. The number average molecular weights of these copolymers were determined using oligomeric gel permeation chromatography (GPC). Polystyrene was used for calibration of molecular weights. The GPC traces of the copolymers are shown in Fig. S1 (ESI[†]), the respective data are summarized in Table 1.

3.2.3 Oligomer synthesis. The well-defined oligomers TTBTT-H and TT(BTT)₂-H were obtained from polymer a-BTT-H ($n = 4$) by preparative GPC after extraction with particular solvents. The crude polymer was extracted sequentially with methanol, ethanol, acetone and methylene chloride. The acetone fraction was used for preparative GPC. Narrow fractions were collected and measured on an analytical GPC setup. Molecular weight analysis of TTBTT-H and TT(BTT)₂-H was done by matrix assisted laser desorption ionization with time of flight detection (MALDI-ToF) mass spectrometry and GPC. The GPC traces and MALDI-ToF spectra of TTBTT-H and TT(BTT)₂-H are shown in the ESI.[†]

4 Influence of the D and A arrangement on the gap

One of the key properties of a low gap system designed for the use in organic solar cells is the optical gap which is defined as the transition energy between the vibrational ground state (GS) of the electronic GS and the vibrational GS of the first excited electronic state. However, more accessible to theory is the vertical excitation energy that is close or identical to the absorption maximum E_{\max} (see Fig. 7). It is the energy

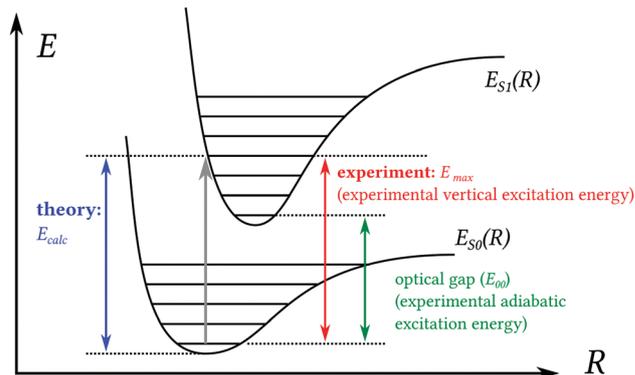


Fig. 7 Schematic of the different excitation energy expressions discussed in this work. R is a generalized coordinate. $E_{S0}(R)$ is the GS energy and $E_{S1}(R)$ the first excited state energy as a function of this coordinate.

difference of the GS and the first excited state with both states in the GS geometry. Hence, the vertical excitation energy is the optical gap (also called adiabatic excitation energy) plus a first or higher order vibrational energy. The energy that we obtain from a standard TDDFT calculation (E_{calc}) is the vertical excitation energy plus the vibrational zero point energy of the electronic GS. This zero point vibrational energy is below the accuracy of the calculation and the error of the experiment and can be neglected. Therefore E_{calc} and E_{max} are comparable. The situation and mentioned energies are illustrated in Fig. 7. In the following, if we write lowest or first excitation energy we mean E_{calc} in a calculation and E_{max} in an experiment.

Our focus in this section lies on the differences between the lowest excitation energies of the DA arrangements a-BTT and r-BTT. These differences directly reveal how large the influence of the DA arrangement on the optical gap is. We calculated these energies for the oligomers $n = 1$ up to $n = 12$ with the RSH approach explained in Section 3, studying one representation of r-BTT for each repeat unit n . The resulting energies E_{calc} are plotted in Fig. 8 as a function of the inverse number of double bonds N^{-1} along the molecular backbone. As discussed in earlier work²⁵ we use an exponential fit to extrapolate to the saturation limit. For the monomer ($n = 1$) both systems are identical. Hence, both curves start at the same point. During the progression to larger N the excitation energies of a-BTT and r-BTT almost overlap each other and saturate at 1.63 and 1.67 eV, respectively. Note that all data points are close to the exponential fitting curves. This confirms that for the purposes of our study it is not necessary to consider different statistical arrangements for r-BTT.

In addition to predicting the saturation energies we can draw two conclusions from this graph. The first one is the saturation length – the amount of repeat units at which the lowest excitation energy saturates. For both systems it lies between $n = 6$ and $n = 8$. The second conclusion concerns the influence of the relative ordering of D and A components on the first excitation energy. Comparing a-BTT with r-BTT we observe that the respective energy values are very close to each other. Thus, the relative order of D and A in the polymer chain has only a minor influence.

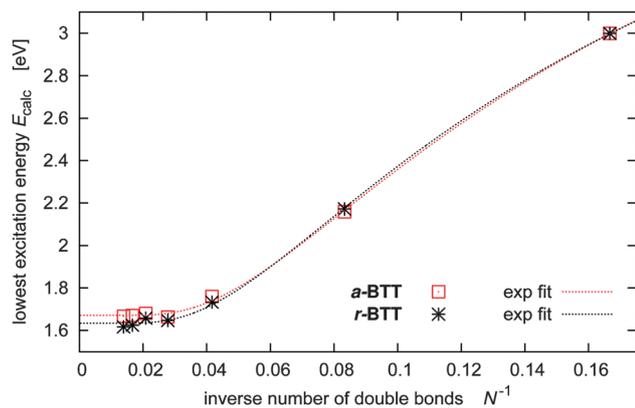


Fig. 8 Lowest calculated vertical absorption energies (TDDFT with tuned BNL and 6-31G(d,p) basis) as a function of the inverse number of double bonds N^{-1} .

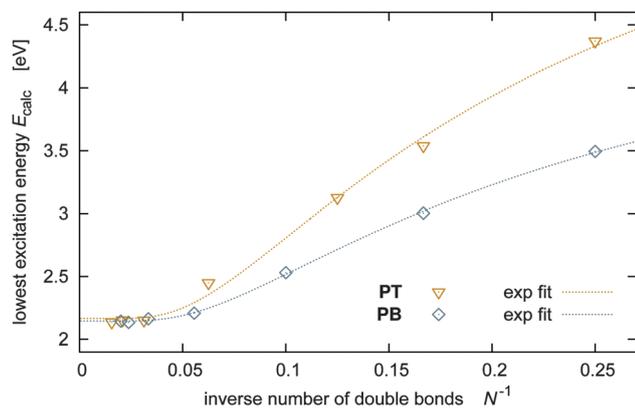


Fig. 9 Lowest calculated vertical absorption energies of T and B oligomers as a function of the inverse number of double bonds N^{-1} .

In order to further elucidate the question of how much the DA arrangement influences the first excitation energy we compare the above results to first excitation energies of oligomers that consist of only either D or A monomers. Fig. 9 shows these energies for T oligomers (PT, $n = 1$ to 32) and B oligomers (PB, $n = 1$ to 25) as a function of the inverse number of double bonds N^{-1} . Both systems coincidentally saturate at a vertical excitation energy of 2.15 eV, which is 0.5 eV above the respective energies of a-BTT and r-BTT. We thus observe the well known effect that combining D and A units reduces the first excitation energy, but in our calculations the magnitude of this reduction is at most 0.5 eV.

Similar conclusions hold when the analysis is extended to not only take the first excitation energies into account, but also the corresponding oscillator strengths and higher excitations. To this end we show the optical spectra of a-BTT and r-BTT for $n = 6$ in Fig. 10. It shows that both systems have very dominant first excitations with oscillator strengths of similar magnitude. Comparing the spectra obtained for different chain lengths (not shown here) confirms that the oscillator strength and dominance increase with n . Besides the main peak the spectra of a-BTT and r-BTT do not show large differences at higher energies. Thus, the calculations show that the conclusions

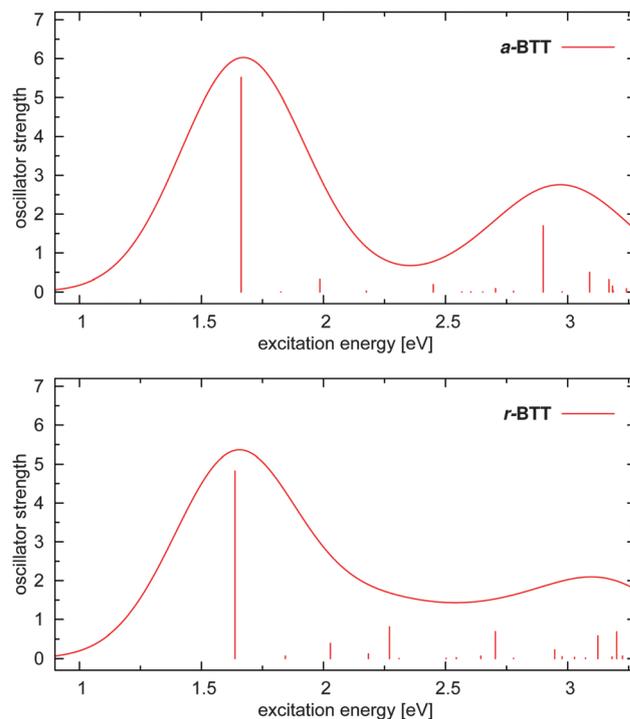


Fig. 10 Calculated electronic excitation spectra of a-BTT and r-BTT with $n = 6$ repeat units (6 B and 12 T units). The calculated positions and oscillator strengths are represented by the bars. Linewidths as present in typical experiments are mimicked by a Gaussian broadening with 0.3 eV HWHM (half width half maximum).

drawn previously for the first excitation energy are valid in a similar way for the overall optical spectrum: the rearrangement of D and A from a-BTT to r-BTT leads to only relatively small changes.

To gain further insight into the physics of these systems we analyze whether CT is important in the lowest excitations. CT excitations are defined as excitations where a transfer of electronic density from one part of a system to another part occurs during the excitation. Typically, CT excitations are prevalent in DA systems since they combine electron poor and electron rich components. In a figurative sense an electron leaves the donor, thus creating a hole, and is absorbed by the acceptor. It is not clear whether this picture holds in DA oligomers or polymers in which the D and A units are distributed along the molecular backbone such that D and A parts are not necessarily adjacent to each other.

In order to examine the CT character of a-BTT and r-BTT we calculated the most dominant natural transition orbital⁴⁶ (NTO) holes and electrons of the first excitation for both systems with a chain length $n = 10$. Fig. 11 (top) shows the most dominant NTO pair for r-BTT accounting for 54% of the excitation. The “hole orbital” and the corresponding “electron orbital” are localized on the same parts of the molecule and are nearly equal in extension. The only difference that we observe is that parts of the electron NTO are located on the sulfur and nitrogen atoms of the benzothiadiazole unit, whereas the hole NTO does not extend to these regions. This difference is so

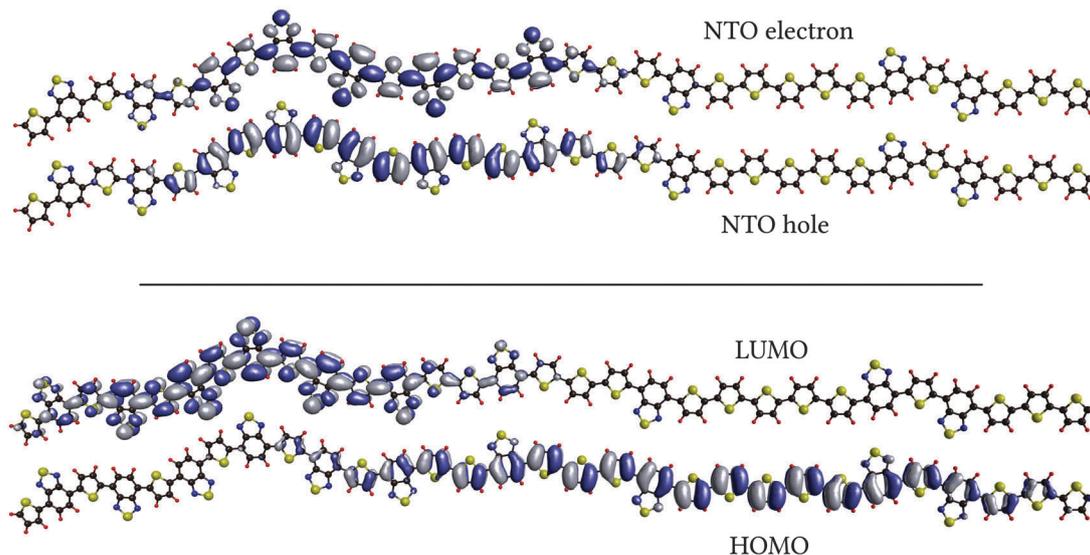


Fig. 11 Most dominant NTO hole/electron of the first excitation (top) and HOMO–LUMO plot (bottom) for r-BTT with $n = 10$. The NTO pair contribution to the excitation is 54% and from the HOMO–LUMO pair 8%. The next three less dominant NTO pairs (accounting for 93% of the excitation) also show no significant CT. The isosurface value is 0.01.

small that this excitation can be classified as having predominantly valence character and just a small CT component. An analysis of the less dominant NTO pairs (shown in Fig. S4 of the ESI[†]) shows that some of these have more CT character, but still overall the excitation appears as being of mixed valence-CT character at most, and not a hallmark CT one. Similar conclusions hold for a-BTT.

In this context it is worthwhile to draw attention to a limitation of the frequently used technique of using HOMO and LUMO orbital plots for analyzing the CT character of an excitation. The present systems are hallmark examples where such a simplified view would lead to even qualitatively wrong conclusions, because many different generalized Kohn–Sham orbital pairs contribute to the lowest excitations. In the case of r-BTT an analysis of the HOMO and LUMO orbitals (Fig. 11 (bottom)) would lead to the conclusion that long-range CT is very dominant here. However, the HOMO–LUMO pair accounts for only 8% of the excitation, *i.e.*, does not suffice to characterize its nature. The other orbital pairs with a significant contribution to the lowest excitation are shown in Fig. S5 of the ESI.[†] Their structure does not allow for clearly assigning a certain character to the excitation.

In the second part of this section, we compare the theoretical results with measurements of a-BTT-H ($\bar{n} = 4, 15$) and r-BTT-H ($\bar{n} = 5, 10$), corresponding to the calculated systems a-BTT and r-BTT. Fig. 12 shows the measured UV/vis spectrum of a-BTT-H and r-BTT-H in chloroform solution and Table 2 compares the maxima of the lowest absorption peaks to our calculated excitation energies. The measured and calculated values for the lowest excitation energy are a good approximation to the vertical excitation energy (*cf.* Section 4). The maxima of absorption for the longer oligomers of a-BTT-H and r-BTT-H are at 2.36 and 2.45 eV, respectively. The small difference with a magnitude of only 0.09 eV is in line with the

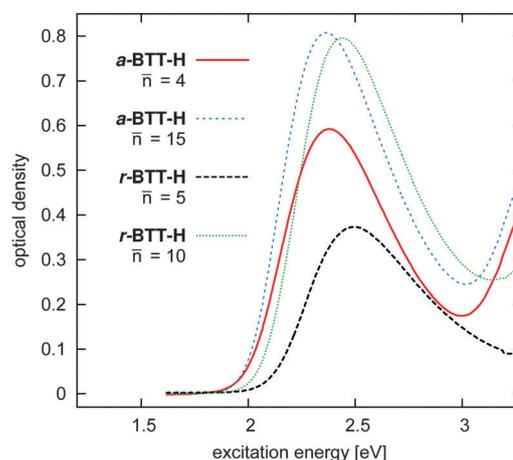


Fig. 12 UV/vis absorption spectra of a-BTT-H ($\bar{n} = 4, 15$) and r-BTT-H ($\bar{n} = 5, 10$) in chloroform solution (0.02 mg ml^{-1}) at room temperature.

theoretical finding that the nature of the arrangement of D and A has only a small influence on the optical gap. Regarding that the difference is not exactly the same – 0.05 eV *versus* 0.09 eV – one has to keep in mind possible small differences between the random arrangements in the calculation and the experiment: in the calculation r-BTT contains exactly twice as many thiophene rings as benzothiadiazole rings, whereas in experiments this ratio can only be achieved approximately.

The most noticeable difference between experiment and theory is found for the absolute values of the excitation energies. The experimental excitation energies are approximately 0.7 eV larger than the theoretical ones, *i.e.*, the difference is considerably larger than what one expects based on the accuracy of the experiments and calculations. We consider our experimental values as reliable since they are in accordance with measurements for similar systems.^{9–11,47,48} One may argue

Table 2 Lowest excitation energies: comparison of an alternating vs. random system in experiment and calculation, respectively. The calculations refer to $n = 12$ for both cases. The experiments refer to $\bar{n} = 15$ for a-BTT-H and $\bar{n} = 10$ for r-BTT-H. In both theory and experiment, the chosen numbers of repeat units lie in the saturated regime (compare Fig. 13 and Section 5)

First excitation energy [eV]			
	Alternating	Random	
	a-BTT	r-BTT	Δ (alt-random)
Calculation	1.67	1.62	0.05
First excitation energy [eV]			
	Alternating	Random	
	a-BTT-H	r-BTT-H	Δ (alt-random)
Experiment	2.36	2.45	-0.09

that it is a well known effect that TDDFT based on local, semilocal or hybrid functionals underestimates CT excitation energies^{25,49,50} and that this may explain the discrepancy. However, because of this reason we use the tuned RSH approach that remedies this problem and is known for very accurately predicting the lowest excitation energies of DA systems.^{16,21,25,26} The discrepancy may thus be regarded as physically significant, and we elaborate on it in the following section.

5 Analysis of the differences between experiment and theory

In order to analyze the disagreement between the theoretical predictions and the experimental data we also synthesized DA systems with a smaller chain length and compared their lowest absorption energies to the corresponding calculated excitation energies. These additionally synthesized systems are BT, TBT-H, TTBT-H, and TT(BTT)₂-H, as schematically represented in Fig. 3. The calculated systems are BT, TBT, TBT-H, TTBT, TT(BTT)₂, and TT(BTT)₂-H, also shown in Fig. 3. We compare the measured and calculated lowest excitation energies in Fig. 13 along with results for the systems a-BTT and a-BTT-H as a function of the number of double bonds N . Additionally, we also show two data points for a-BTT with methyl side chains (indicated by “M” in the graph). In the left part of the graph (small systems) we have good agreement between theory and experiment. If the difference between theory and experiment were to be attributed solely to unreliability of the theoretical predictions, then the tuned RSH would have to be accurate for small systems but systematically fail for larger ones – a scenario that we do not consider likely, at least not in the size range studied here, given the previously published results obtained with the tuned RSH approach. We also note that the experimental values are in line with measurements of other, similar systems.^{8,52–55} Yet, as

§ B3LYP calculations would result in an even lower gap. For a-BTT one would obtain a saturated lowest excitation energy of 1.33 eV, 0.34 eV lower than our tuned BNL calculations.

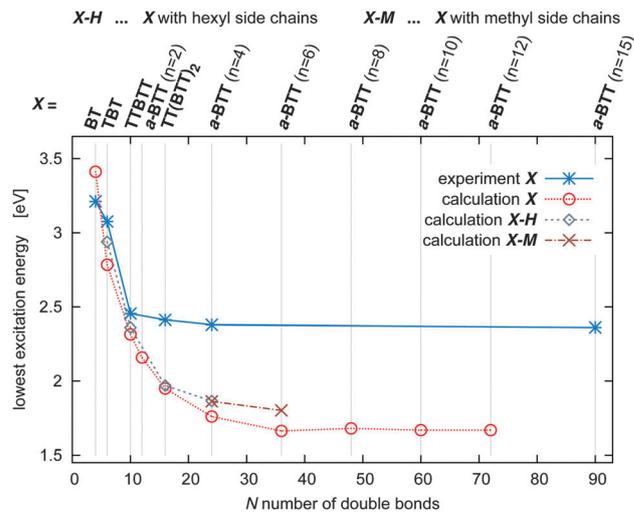


Fig. 13 Lowest excitation energies as a function of the number of double bonds N . The experimental data points reflect the maxima of the UV/vis spectra. The calculated data points are obtained from tuned BNL TDDFT linear response calculations. The dotted lines are drawn as guides to the eye. All systems in the experiment have hexyl side chains (C_6H_{12}) attached to the thiophene rings as shown in Fig. 2 and 3; for the calculations we show data points for systems with hexyl and methyl side chains⁵¹ and compare them to systems without side chains.

the systems get larger the difference between the experimental and the theoretical results increases.

In the experiment, the B units can have neighboring T units with hexyl chains pointing inwards, away, or in both directions. This can happen because during the synthesis the orientation of the bithiophene can change from one B to the next B unit (*cf.* Fig. 6). To examine the consequences that the different side-chain orientations can have we calculated the excitation energy for TBT with asymmetrically and symmetrically attached side chains. In the symmetric case the side chains point inwards and as a consequence lead to larger torsion angles between the thiophene and benzothiadiazole units. Furthermore, the chains are spatially closer and can therefore interact more. In line with this reasoning we observe in Fig. 14 that indeed in the symmetric case ((ii) in Fig. 14) the excitation energy changes by 0.15 eV whereas the changes are negligible for the asymmetric case ((i) in Fig. 14). Fig. 13 shows results that were obtained for different molecules with hexyl (H) and methyl (M) side chains attached as schematically shown in Fig. 2 (left side), *i.e.*, one of the neighboring T rings has a side chain pointing towards the B unit and the other pointing away. We chose this configuration in the calculations because it occurs on average in the experiment since the hexyl chains on the bithiophene units are asymmetrically attached (*cf.* Fig. 6). The lowest excitation shifts by at most 0.15 eV towards the experimental value. In summary these results indicate that the influence of the side chains may be able to explain part of the discrepancy between theory and experiment, but not all of it.

One possibility which we so far did not take into account and which may play a role in explaining the discrepancy are interactions between the systems and the solvent that may change the experimental excitation energies. Therefore, we explored the

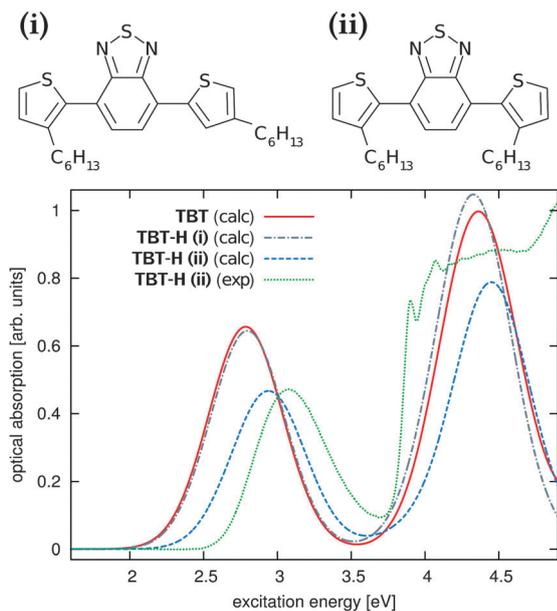


Fig. 14 Comparison of the calculated spectra (calc) for TBT and TBT-H and the UV/vis experimental spectrum (exp) for TBT-H in chloroform solution (0.02 mg ml⁻¹) at room temperature. For TBT-H we calculated a system with asymmetrically (i) and symmetrically (ii) attached hexyl side chains. Only case (ii) is examined in the experiment. As a guide to the eye the calculated peak positions are broadened with 0.3 eV HWHM and the measured optical density (experiment) is multiplied by a factor chosen to equalize the peak heights of the first peak of TBT-H (ii) in experiment and calculation.

influence of the solvent on some of the smaller systems. In the calculations, the solvent (as modeled by the solution model) has only little influence on the structure during geometry optimization. It also influences the excitation energies very little; the overall effect is less than 0.04 eV. Hence, solution models (*cf.* Section 3) cannot explain the large differences between experiment and theory. Also, the direct electronic effects of a solvent (*e.g.*, screening) should influence small and large systems in a similar way. On the experimental side we explored the effects of using different solvents. Besides chloroform we also measured the UV/vis spectrum of r-BTT-H with tetrahydrofuran and toluene. The observed shifts of the absorption maximum are less than 0.02 eV, *i.e.* very small. Thus, the discrepancies between experiments and calculations are not solvent dependent or at least similar for all tested solvents.

Another possibility is that the experimental geometries are more distorted than the stretched geometries that we used in the calculations (*cf.* Fig. 4). Although changing the orientation of the T vs. the B unit has only a small local influence on the structure (different cases have been discussed, *e.g.*, in ref. 56 and 57), it can change the global curvature of a chain, *e.g.*, from a stretched to a curved geometry. For r-BTT we constructed such a curved structure by choosing the sulfur atom of thiophene to always point in the opposite direction of the sulfur atom in benzothiadiazole. The optimized geometry of this system is displayed in Fig. 15. Compared to the stretched structure the excitation energy of this system changes by about 0.05 eV. This demonstrates that a globally curved structure can reach nearly as low a gap as a straight structure.

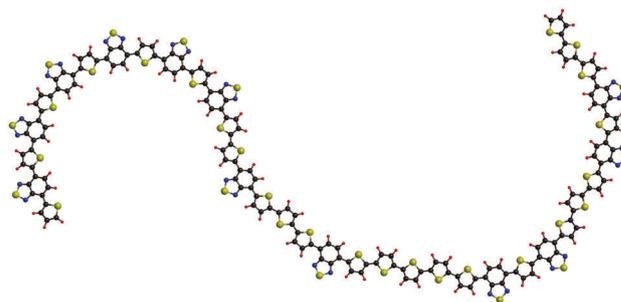


Fig. 15 Example of a curved structure for r-BTT with $n = 12$. Fig. 4 shows an example of a stretched version of r-BTT.

Another reason that could explain the discrepancy between theory and experiment is a difference in the effective conjugation length. Fig. 13 shows a significant difference in how the experimental and theoretical curves saturate with increasing system size. The experimental excitation energies already start to saturate at a number of double bonds of $N \approx 15$, whereas in theory the saturation is at $N \approx 35$. This corresponds to a BTT repeat unit of $n \approx 3$ for the experiment and $n \approx 6$ for theory. This result might not be unexpected, however, its extent is worrisome and may well explain that the minimal achievable lowest excitation energy in the experiment is 0.7 eV above the calculated saturated energy. There are different factors that may lead to an effective limitation of the conjugation length in the experiments. Likely candidates are interactions between different chains and between chains and the solvent, which may lead to kinks and torsions in the structure and may thus break the electronic conjugation along the molecular backbone. The effect could be intensified by the hexyl chains that are attached to the structures in the experiment.

Thus, the results for all our systems, which cover both the well defined small molecule range as well as the oligomeric/polymeric range, can be summarized as follows. For the case of small molecules, there is full agreement between theory and experiment. In the range of oligomers and polymers the theoretically found (first) excitation energies are by *ca.* 0.7 eV smaller than the ones found experimentally. However, the theoretical and the experimental results for the optical absorption agree with respect to the finding that different D and A arrangements lead to very similar excitation spectra. We extensively discussed the effects that can contribute to the 0.7 eV difference, and this brings us to our conclusion.

6 Conclusion

We studied theoretically and experimentally the influence that the relative ordering of D and A units has on the optical absorption of DA systems consisting of thiophene and benzothiadiazole. The lowest excitation energy changes only very little (<0.1 eV) in our TDDFT calculations based on a tuned RSH functional when going from the alternating to the randomly arranged DA system. This result was confirmed by our experimental study. Analysis of the NTOs showed that long-range CT is

not dominant in the first optical excitation. Our calculations predicted the lowest possible excitation energy for a-BTT to be 1.67 eV with a saturation length of approximately 6 BTT repeat units. A comparison with measured excitation energies from a solution measurement reveals that the excitation already starts to saturate after 3 repeat units of BTT. Although the synthesized systems can have 15 repeat units or even more, they behave like oligomers with 3 BTT repeat units with respect to the optical properties. Thus, the maximum conjugation length in experiments is much lower than what appears to be theoretically achievable. Correspondingly, the minimum achievable optical gap is 2.36 eV, *i.e.*, *ca.* 0.7 eV larger than the theoretical prediction. Effects that may cause this discrepancy between the experiment and the theoretical prediction were discussed and, in agreement with work on other DA systems,^{56,57} we conclude that future work may need to go beyond the single molecule level. Such work could provide further guidance in the design of oligomers or polymers that have the effective conjugation length that is necessary for a lower optical gap.

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