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Dipole Moment and Polarizability of Tunable Intramolecular Charge Transfer States in Heterocyclic π -Conjugated Molecular Dyads Determined by Computational and Stark Spectroscopic Study

Egmont J. Rohwer^{*,†}, Maryam Akbarimoosavi[†], Steven E. Meckel[‡], Xunshan Liu[§], Yan Geng[§], Latévi Max Lawson Daku^{||}, Andreas Hauser^{||}, Andrea Cannizzo[†], Silvio Decurtins[§], Robert J. Stanley[‡], Shi-Xia Liu[§], Thomas Feurer^{*,†}

[†]Institute of Applied Physics and University of Bern, 3012 Bern, Switzerland [§]Department of Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland [‡]Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, United States ^{||}Department of Physical Chemistry, University of Geneva, 1211 Geneva, Switzerland

Abstract

The annulation of two redox-active molecules into a compact and planar structure paves the way toward a new class of electronically versatile materials whose physical properties can be tuned via a substitution of one of the constituting moieties. Specifically, we present tetrathiafulvalene–benzothiadiazole donor–acceptor molecules. The critical role played by the dielectric properties of these molecules is evident by the large spectral shifts of the ground-state absorption spectra in a range of solvents. Stark spectroscopy is performed to determine experimentally dipole and polarizability change over transitions in the visible range with particular attention to the transition from the highest-occupied molecular orbital (HOMO) to the lowest-unoccupied molecular orbital (LUMO). The experimental results are compared to the results of time-dependent density functional theory calculations, and we reciprocally validate results from calculation and experiment. This allows us to filter out effective models and reveal important insights. The calculations are initially performed in the gas phase and subsequently a polarizable continuum model is adopted to probe the influence of the solvent on the molecular dielectric properties. The results show a large charge displacement from the HOMO to the LUMO and confirm the intramolecular charge transfer nature of the lowest-energy transition. Substitution of the acceptor moiety with electron-withdrawing groups results in changes to the experimentally determined molecular properties consistent with the effects predicted by computational results. The dominant contribution to the electroabsorption signal is due to the change in dipole moment, which is

^{*}Corresponding Authors egmont.rohwer@iap.unibe.ch (E.J.R.), thomas.feurer@iap.unibe.ch (T.F.).

Supporting Information

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Stark spectra and data fitting for TTF-BTD_H and TTF-BTD_{CN} and relevant material parameters (PDF)

The authors declare no competing financial interest.

measured to be roughly 20 D for all samples and forms a small angle with the transition dipole moment in a toluene solvent environment.

Graphical Abstract

INTRODUCTION

Heterocyclic tetrathiafulvalene (TTF)¹⁻⁵ and benzothiadiazole (BTD)⁶⁻⁸ moieties that are covalently fused to form single planar π -conjugated molecules (Figure 1) have several promising properties for adoption in molecular electronic devices. The generation of an energetically low-lying intramolecular charge transfer (CT) state and highly polarizable molecules through the annulation of strong electron donor and acceptor moieties is of prime interest.⁹⁻¹³ The highest-occupied molecular orbital (HOMO) of the molecular dyad is spatially localized on the donor fragment and the lowest-unoccupied molecular orbital (LUMO) on the acceptor part. Consequently, the electron-donating properties of TTF and, conversely, electron-accepting properties of BTD create a low energy band gap material¹⁰ because of the intramolecular CT nature of the HOMO–LUMO transition.^{9,11} Substitution of the 4 and 8 positions of the BTD moiety allows for fine tuning of the band gap by variation of the LUMO energy level.^{14,15} This allows the resulting molecule to have p-type semiconductor properties in the case of Br substitution or, if the LUMO is lowered further by CN substitution, ambipolar semiconducting properties. To note, through annulation of strong electron donors and acceptors into a single molecular dyad, an electrochemical HOMO–LUMO gap as low as 0.5 eV can be achieved.^{12,13}

An accurate picture of the dielectric properties and charge distribution within these molecules is useful when considering materials for applications such as those outlined above. In this work, we compare theoretical calculations of properties such as dipole moment and electric dipole polarizability with measurements of the change in dipole moment and polarizability over the HOMO–LUMO transition, obtained by Stark spectroscopy.

Optical Stark spectroscopy^{16,17} is a powerful method to obtain changes in charge distributions upon electronic excitation. The application of an external electric field has its largest effect on states where the charge redistribution is large. In the case of change in dipole moment in an $S_0 \rightarrow S_n$ transition, μ_{0n} , the measured signal is proportional to $|\mu_{0n}|^2$. Thus, CT transitions that are usually broad or difficult to distinguish from non-CT transitions are well-resolved and easily identified. A recent example is that of a CT dyad consisting of an azobenzyl donor group flavin tethered to the C8 position of N10-isobutylflavin.¹⁸ The largest optical absorption band had a $|\mu|$ of over 23 D, with an accompanying large difference isotropic polarizability ($\text{Tr } \alpha$) of over 1200 Å³.¹⁹ For purposes of comparison, the flavin by itself has $|\mu| \approx 2$ D and a very small $\text{Tr } \alpha$ for its lowest $\pi-\pi^*$ transition.²⁰ Other “push–pull” molecules with large nonlinear optical properties have also been studied by Stark spectroscopy.^{21–23}

The samples investigated here are TTF–BTD dyads with H, Br, and CN groups substituted at the 4 and 8 position of BTD to create a sample set labeled **1**, **2**, and **3**, respectively. By achieving greater insight into the movement of charge when the molecule undergoes the HOMO–LUMO transition characterized by CT, further optimization of the material for specific functions can be undertaken.

EXPERIMENTAL METHODS

Sample Preparation.

The compounds **1–3** were prepared according to methods described in the literature.^{10,14,15}

Computational Details.

The geometries of the molecules were optimized within density functional theory (DFT), using the Perdew–Burke–Ernzerhof (PBE) functional²⁴ and the def2-TZVP basis set.²⁵ In all cases, the molecular symmetry was kept fixed to C_s . The frequency calculations performed on the optimized geometries showed that they correspond to true minima (no imaginary frequencies). For each molecule, the characteristics of the $S_0 \rightarrow S_{n-1}$ electronic transitions were determined within linear response theory in time-dependent DFT (TD-DFT),^{26–28} using the PBE0 functional²⁹ and the def2-TZVP basis set. Note that the PBE0/def2-TZVP level was selected after assessing the performances of different functionals and basis sets for accurately predicting the excited state properties of the three molecules. For the molecules in the S_0 state, the electric dipole moment and the isotropic polarizability were calculated at the PBE0/def2-TZVP by finite differences. The electronic excitation calculations required for the finite-difference method were performed in C_1 . The aforementioned calculations were done for the molecules in the gas phase. To probe the influence of the solvent on the dielectric properties of the molecules, the calculations were also performed in toluene using the polarizable continuum model (PCM) of solvation.³⁰ All calculations were performed with the Gaussian 09 program package.³¹

Stark Spectrometer.

A detailed description of the experimental setup can be found in the literature,¹⁹ but a general overview is provided by the schematic in Figure 2. A Xe arc lamp and a 1/8 m

monochromator with 2 nm bandpass form the light source. Polarization of the probe light can be set with a Glan–Taylor prism. The light is passed through a double-reservoir dewar (Janis, based on a prototype by Andrews & Boxer)³² that houses the sample. The sample itself is contained in a user-assembled sandwich cell consisting of indium tin oxide-coated glass with conducting sides facing each other. Kapton spacers of 25 μm thickness separate the plates and form a cavity that can be filled with solution by injection. Wires ending in crocodile clamps are attached to each of the plates and allow a potential to be applied resulting in an electric field between the conductive sides of the glass plates. A peak potential of 354 V results in a peak electric field strength of 140 kV/cm in the space between the plates. The sandwich cell can be rotated about a vertical axis within the dewar by a connecting rod to the outside to facilitate changes in the relative angle between the applied field and the probe light polarization. By filling the dewar with liquid nitrogen, the sample is cooled to 77 K. The rapid freezing results in an optical glass if an appropriate solvent is used. The freezing immobilizes the sample, simplifying the model needed to analyze the data and has the added advantage of resulting in spectrally narrower absorption features. Because Stark effects are observed as shifts in wavelength of the absorption features, narrower features make any shift easier to detect. Light that is transmitted by the optical glass is focused onto a silicon photodiode. The resulting signal is processed through a current-to-voltage amplifier and measured by lock-in amplification at twice the frequency of the applied ac-field, allowing for detection of the perturbed transmission intensity, I . Finally, the photovoltage is read by a 16-bit A–D converter to supply the needed reference intensity, I_0 , and the ratio I/I_0 is converted to ϵ as described elsewhere.³³ The sine wave generator of the lock-in amplifier provides the master clock and modulates the applied potential to the sample cell at 3.5 kHz.

Analysis of Stark Data.

Data from the Stark spectrometer are interpreted in terms of the Liptay formalism.¹⁷

$$\frac{\Delta\epsilon(\tilde{\nu})}{\tilde{\nu}} = (f_c |\vec{F}|)^2 \left\{ A_\chi \frac{\epsilon(\tilde{\nu})}{\tilde{\nu}} + \frac{B_\chi}{15ch} \frac{d}{d\tilde{\nu}} \left(\frac{\epsilon(\tilde{\nu})}{\tilde{\nu}} \right) + \frac{C_\chi}{30c^2h^2} \frac{d^2}{d\tilde{\nu}^2} \left(\frac{\epsilon(\tilde{\nu})}{\tilde{\nu}} \right) \right\} \quad (1)$$

The model is suited to samples with an isotropic distribution of transition dipole moments. This is the reason for immobilizing the sample in the experimental setup. The measured spectrum is fitted with terms consisting of the energy-weighted extinction coefficient spectrum ($\epsilon(\nu)/\nu$) and its first and second derivative as variables. These components are weighted in a linear combination by the coefficients A_χ , B_χ , and C_χ for the zeroth, first, and second derivative term, respectively. According to the model, the A_χ coefficient is determined by the transition polarizability and transition hyperpolarizability properties of the sample. For immobilized samples, these contributions are often small and in this case were found to be within the noise level of the measurement. The B_χ coefficient is related to the change in polarizability from the ground to excited state and is formally represented as

$$B_{\chi} = \frac{5}{2} \text{Tr} \Delta \alpha + (3 \cos^2 \chi - 1) \left(\frac{3}{2} \vec{m} \cdot \Delta \alpha \cdot \vec{m} - \frac{1}{2} \text{Tr} \Delta \alpha \right) \quad (2)$$

where $\text{Tr}(\alpha)$ is the trace of the difference polarizability tensor, $\vec{m} \cdot \alpha \cdot \vec{m}$ is the projection of the tensor onto the direction of the transition dipole moment, and χ is the experimental angle between the applied field and probe polarization. The C_{χ} coefficient is mainly affected by the change in dipole moment (μ) over the transition.

$$C_{\chi} = |\Delta \vec{\mu}|^2 \{5 + (3 \cos^2 \chi - 1)(3 \cos^2 \zeta - 1)\} \quad (3)$$

ζ represents the angle between the change in dipole moment and the transition dipole moment. Because both B_{χ} and C_{χ} are functions of the angle χ between the incident probe light polarization and the applied electric field, two spectra are needed to uniquely solve for all variables. By using the Glan–Taylor prism, we set the incident polarization of the probe light in two separate measurements to be orthogonal to each other. Because of the geometry of the setup, a vertically polarized incident beam is always orthogonal to the applied field and in the case of a horizontally polarized probe beam this relative angle can be adjusted by rotating the cell about the vertical axis.

Fitting Procedure.

To fit the data according to the Liptay model, an accurate low temperature energy-weighted extinction coefficient spectrum is required. This is obtained in the same setup as described above without the applied field and with thicker Kapton spacers. The monochromator selects probe wavelengths in intervals equal in energy, that is, linear in wavenumber, and the photodiode registers a transmission value. This is done for the sample and a reference containing only the solvent. By adding parameters such as concentration and sample length, the required spectrum expressed in terms of extinction coefficient can be calculated. The result is fit with a sum of Gaussian functions for each transition of the sample. The collection of Gaussians represents each of the sample's individual transitions in the spectral window they appear in and can be manipulated to achieve a better fit. The constituent Gaussians have no physical meaning and as many are used as is necessary to achieve a satisfactory fit to the low-temperature absorption spectrum. The fit results in a smooth function where first and second derivatives are obtained analytically, avoiding the noisy unusable result of a numeric procedure. The fit to the absorption spectrum and its derivatives are used to fit the results of the Stark measurements with the terms in eq 1 simultaneously. Parameters such as applied voltage, cell thickness, and probe polarization need to be entered for proper normalization of the Stark spectrum. For comparison, all Stark spectra are normalized to 1 MV/cm field strength. After a good fit has been achieved values for $\text{Tr}(\alpha)$, $\vec{m} \cdot \alpha \cdot \vec{m}$, μ , and ζ for each transition can be extracted. Up to 200 iterations of Monte Carlo simulations, in which the starting values for each parameter are varied, are performed. This allows the user to check the robustness of the fitted parameters by how often the parameters

converge after the fitting procedure. We present each parameter as the mean value from all successful iterations as well as the standard deviation for each value.

RESULTS

DFT Results.

For each of the three molecules, the lowest-energy absorption band can be assigned to the $S_0 \rightarrow S_1$ electronic transition, which corresponds to a HOMO $\rightarrow$ LUMO transition and which can be viewed as a TTF $\rightarrow$ BTB transition. Within the series, the HOMO–LUMO energy gap is predicted to decrease in the order: (H) > (Br) > (CN), that is, sample **1** > sample **2** > sample **3**. The predicted energies, wavelengths, and oscillator strengths associated with absorption from the ground state to S_1 state are summarized in Table 1. Major molecular orbital contributions to the $S_0 \rightarrow S_1$ transition for all samples along with the results for higher lying transitions for the Br-substituted sample (**2**) can be found in the Supporting Information (Figures S1 and S2).

Electric dipole moments, transition dipole moments, and polarizabilities of the S_0 and S_1 state of all samples are summarized in Table 2. The directions within the molecular framework that the axes were chosen to point in are illustrated in the Supporting Information (Figure S3). Generally speaking, the y -axis runs parallel to the long molecular axis in all samples. Calculations were done to determine a bend angle between the two 1,3-dithiole rings in the optimized geometry for gas phase. We define this angle as the relative inclination of the planes formed by 1,3-dithiole rings on either side of the C=C bond in TTF. This is best illustrated by the images in Figure S3 in the Supporting Information. The result was an angle of 39.0° for the unsubstituted sample **1**, a smaller angle of 35.2° for the Br-substituted sample **2**, and an even smaller angle of 29.7° for the CN-substituted sample **3**. This shows a clear correlation with the calculated energy of the samples' $S_0 \rightarrow S_1$ transition.

Modeling Interaction with Toluene.

The calculations were performed again for the molecules in toluene using the PCM of solvation. The inclusion of solvent effects led to a marginal change of the molecular geometries. It however translated into an increase of the ground and excited dipole moments, as summarized in Table 3. These calculations were repeated using the gas phase geometries, and the results showed only minor changes, indicating that the increased dipole moments resulting from these calculations are chiefly due to the simulated solvent effects. With the PCM, specific short-range solute–solvent interactions are missing which may lead to geometries that substantially differ from the predicted ones. To test how these interactions may produce different results, we forced a change in geometry by varying the bend angle and partially optimizing the molecular geometry around it. Then, we ran the calculations again for the new geometry. We did this for five different bend angles per molecule and evaluated the data. We compared the results for three parameters of specific interest, namely, the energy of the HOMO–LUMO transition, the associated change in dipole moment, and the associated change in isotropic polarizability, in Figure 3.

Absorption and Stark Spectra.

In the remaining part of this section, we report on the Stark spectroscopy results. We focus on a detailed account of the results for one of the molecules at every stage of the data processing protocol as outlined in the Experimental Methods section to clearly state the assumptions made and the experimental considerations that need to be taken into account. Because the molecules are very similar in structure and chemical character, we only present the relevant physical quantities extracted from the processing of the data for the remaining molecules in the Discussion section. We demonstrate with results from the Br-substituted TTF-BTD (sample **2**) as it showed the largest response because of the high field achieved in the experimental setup for this sample. As shown in Figure 4, the lowest-energy absorption band is at an intermediate position and more separated from the absorption band for higher lying states than the unsubstituted sample **1** and well within the spectral observation window, unlike the absorption of the CN-substituted sample **3** which is clipped at the low energy edge of the spectral probe window. The fitting of the data therefore proved to be more robust, and the Monte Carlo simulations converged more reliably. The results for the remaining samples can however be found in the Supporting Information (Figures S4-S12).

The low temperature absorption spectrum of sample **2** is shown in Figure 5. We select the wavelength region from the red edge (750 nm/13 300 cm^{-1}) of the experimental window to 700 nm (14 300 cm^{-1}) as the baseline where the sample does not absorb. The Stark spectra for the sample taken with different relative angles between probe polarization and field are shown in Figure 6. The region between 300 (33 300 cm^{-1}) and 750 nm (13 300 cm^{-1}) is selected for the fitting of the low temperature absorption spectrum and the two Stark spectra. As before, the spectral window between 750 and 700 nm is selected as the baseline because no Stark signal is detected there.

To fit this absorption spectrum, the region centered about the peak absorption at 500 nm/20 000 cm^{-1} is assigned to a single HOMO-LUMO transition. DFT calculations predict several transitions to contribute to the absorption on the blue side of 400 nm/25 000 cm^{-1} but only two with significant oscillator strength (see Supporting Information Figure S2). We approximate this by selecting two further bands to fit the absorption of transitions in the region stretching roughly from 400 to 350 nm (25 000–28 500 cm^{-1}) and from 350 to 300 nm (28 500–33 300 cm^{-1}), taking the observed solvatochromic blue shifts into account. This is done to separate the Stark effect induced in the HOMO-LUMO transition from the effect of higher lying bands particularly for the overlap region between 400 and 450 nm (25 000–22 200 cm^{-1}). The different electrochromic responses due to different probe polarizations in three distinct regions centered around 19 000, 25 500, and 29 000 cm^{-1} in Figure 6 strongly suggest that three optically allowed transitions with distinct electronic structure comprise the optical transitions within the Stark probe window. Because the HOMO-LUMO transition is, from an applications perspective, of particular interest, it should be noted that a control fitting was done with a single transition for the region 450–750 nm (22 200–13 300 cm^{-1}) and yielded similar results.

The result of the simultaneous fitting algorithm for Stark and ground-state absorption spectra produced a good fit to the low-temperature absorption spectrum (see Figure 5) with a well-

defined band stretching around the central absorption wavelength caused by the HOMO–LUMO transition. Figure 6 shows the fit to the Stark spectra. Figure 7 shows a breakdown of the contribution from zeroth, first, and second derivative components of the low-temperature ground-state HOMO–LUMO transition. As expected for immobilized samples, an insignificant contribution from the zeroth order is observed. The dominant contribution is from the second-order derivative line shape in the spectral absorption region corresponding to the HOMO–LUMO transition. The higher lying transitions are fitted with a more balanced contribution from the first and second order derivative lineform.

In Figure 8 we show a breakdown of the contributions to the Stark fit of all three ground-state transitions that were fitted in the low temperature energy-weighted extinction coefficient spectrum of Figure 5.

A run of 200 Monte Carlo simulations provides a measure of confidence in the extracted parameters. These converged reliably for all three transitions and for all the parameters, that is, change in dipole moment (μ), the angle between transition dipole moment (m) and difference dipole moment (μ) denoted by ζ , the trace of the difference polarizability tensor ($\text{Tr}(\alpha)$), and the projection of the difference polarizability tensor on the transition dipole moment ($m \cdot \alpha \cdot m$). The single exception is the ζ parameter for the highest energy transition. The results are summarized in Table 4.

DISCUSSION

The discrepancy between the observed peak absorption wavelength for the HOMO–LUMO transition at room temperature and the calculated value is within the bandwidth of the observed transition for all three samples, indicating a good correlation between experiment (Figure 4) and calculation (Table 1). The TD-DFT calculations were done for the gas phase. The solvatochromic effect of the solvent toluene offers potential for some discrepancies. Additionally, just as with the oscillator strength in the TD-DFT calculations, the peak molar absorptivity of the HOMO–LUMO transition is similar for all samples.

Comparison with Stark Spectra: HOMO–LUMO Transition.

Fitting of the experimental Stark spectra in the HOMO–LUMO transition region shows a dominant contribution in all cases from the second-order derivative line shape of the low-temperature energy-weighted extinction coefficient spectrum (Figure 7 and Supporting Information Figures S10–S12), which is primarily a result of the linear Stark effect. The low error estimation for the change in dipole moment for all samples reflects this. This is in agreement with TD-DFT calculations which predicted large changes in dipole moment in a narrow range of values. There is particularly good agreement for the experiment with the Br-substituted sample, which yielded the best Stark signal, with the DFT calculations. The measured change in dipole moment from HOMO to LUMO is $19 \text{ D} \pm 1$, which should be compared to the calculated value of 12.98 D in gas phase and 16.199 D if the PCM is applied to simulate the solvent effect.

The error in the estimation of the isotropic change in electric dipole polarizability from HOMO to LUMO is substantially larger with a value of $200 \text{ \AA}^3 \pm 50$ for the parameter

$\text{Tr}(\alpha)$. The corresponding value in the gas phase resulting from DFT calculations corresponds to an increase of only 7 or 12 Å³ if we take the solvent into account. The considerable difference in absolute value may have to do with how the solvent environment is modeled and the fact that the contribution of the Stark effect due to the difference in polarizability is fitted as a small change to the overall Stark effect dominated by the change in dipole moment. The relative noise level for this contribution increases correspondingly. The experimental results confirm the predicted increase in polarizability for the sample over the HOMO–LUMO transition that manifests as a red shift of the absorption band due to an applied field. In a heterodyne detection scheme, this appears as a positive first derivative line shape as in the Stark spectrum of Figure 7.

From the DFT calculations, a further parameter could be extracted and compared to experimental results. The parameter μ was found to be more or less parallel to the y -axis, forming an angle of 0.5–3°, with smaller values for sample **3** and larger ones for sample **1**. Likewise, the transition dipole moment was found to point obliquely along the y -axis for samples **1** through **3** (3.5–7°, reflecting the same trend of smaller angles for sample **3** and larger for sample **1**). As pointed out by Mulliken, CT bands are characterized by nearly parallel transition and difference dipole moments.³⁴ In the Liptay formalism, this can be extracted from the experimental data by determining ζ . A perfect CT transition would have $\zeta = 0^\circ$. Reliable information can be extracted from the data, because the signal is well-resolved and shows a clear dichroism in the HOMO–LUMO transition region in the two measurements with a 52° angle between probe and applied field in one case (38° incidence) and orthogonal directions in the other (Figure 5). The value obtained from the fits for this sample is $23^\circ \pm 6$. Of course, under experimental conditions, the samples are subject to electrostatic interactions with the toluene environment. At room temperature, the solvent causes fluctuations in the molecular geometry, and a frozen distribution of these geometries is sampled in the experiment at low temperatures. The Stark signal is sensitive, as eq 3 shows, to the absolute value of ζ but not the sign. For this reason, we interpret the value ζ as a standard deviation for the angle formed between the transition dipole moment and difference dipole moment over a distribution of possible molecular contortions that the solvent can induce. Rapid freezing of the sample in the experimental setup preserves this distribution. We deduce that the measured distribution is largely of geometries approaching the optimized structure that show CT with parallel transition dipole and difference dipole moments and result in the observed large dipole change. The distribution includes, however, deviations from the optimized structure that cause contributions from donor-localized transitions where the orientation of the transition dipole can vary and, presumably, the dipole change is small. The overall result is a large dipole change with fixed orientation and a ζ parameter that is nonzero because of the distribution of transition dipole moment orientations but small because the distribution is weighted toward the parallel orientation of dipole change and transition dipole moment. The discrepancy between the observed experimental value and the value obtained from DFT calculations in gas phase may also be affected by the distortion of the charge distribution induced by the frozen solvent. The effect is absent in gas phase and is considered only perturbative in simulations that consider the presence of a solvent.³⁵

Comparison with Stark Spectra: Other Transitions.

TD-DFT calculations predicted two other transitions in the UV region with similar oscillator strength to the $S_0 \rightarrow S_1$ /HOMO–LUMO transition and a comparable change in dipole moment. Calculations show these to absorb at 340 and 293 nm in the gas phase for the Br-substituted sample (Supporting Information Figure S2). We observe two transitions that fit this description in our fit to the low-temperature absorption spectrum of Figure 5 and show a signal in the corresponding region of the Stark spectra. A weaker donor-localized transition that calculations assigned to the $S_0 \rightarrow S_3$ transition in the region around 390 nm is observed in the ground-state absorption spectrum but does not seem to be active in the Stark spectrum and is therefore not considered by the fitting algorithm. The fitting of the low-temperature absorption spectrum seems to include this absorption feature in the HOMO–LUMO band. If we look at the details of the TD-DFT calculations, we see that the transition at 340 nm corresponds to an $S_0 \rightarrow S_5$ transition with a molecular orbital contribution coming from the LUMO in the upper level and an orbital localized on the TTF moiety below the HOMO in the lower level. The difference in dipole moment is therefore also high, 9.96 D. The transition dipole moment also points roughly along the long molecular axis but forms a slightly larger angle of 7° with the y -axis than HOMO–LUMO (5°). The change in dipole moment also forms a slightly larger angle with the y -axis than in the case of the HOMO–LUMO transition. The transition predicted by calculation to absorb at 290 nm corresponds to an $S_0 \rightarrow S_9$ transition. In the Supporting Information, we see that this has two significant molecular orbital contributions where, in both cases, the lower level is HOMO and the upper levels are different molecular orbitals distributed broadly (and less-broadly) around the C–C double bond of the TTF moiety. Perhaps in agreement with intuition, the dipole change from $S_0 \rightarrow S_9$ is calculated to be 3.34 D, less than for $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_5$. We observe that experimental results also show strong contributions from the linear Stark effect in the spectral regions associated with these transitions. The intermediate transition resulting from the fit to the low temperature absorption spectrum with a peak at 340 nm (dashed line in Figure 5) has a large second-order derivative line shape contribution to the Stark spectrum as shown by the green dotted line in Figure 8. The same can be said of the optical transition on the blue side of 330 nm, which is shown by the dash-dotted line in Figure 5 and which has Stark contributions shown by the blue lines in Figure 8. Having identified these transitions, we can compare the dipole change extracted from the fits to the data to those calculated for $S_0 \rightarrow S_5$ and $S_0 \rightarrow S_9$. These values, from Table 3, are $10 \text{ D} \pm 2$ for the former and $3 \text{ D} \pm 1$ for the latter. The calculations predicted a larger difference in polarizability for these transitions (Supporting Information) than for the HOMO–LUMO transition. The increased role that the dash-dotted lines play in fitting the Stark spectrum in the corresponding spectral regions attests to this. For the transition that we have identified as $S_0 \rightarrow S_5$, we also fit a value for ζ of $32^\circ \pm 10$, roughly the same as for $S_0 \rightarrow S_1$ ($23^\circ \pm 6$). The calculations also showed a minimal change for this parameter.

Effect of Substitution with H and CN on the Acceptor Moiety.

For technical reasons that are outlined in the Supporting Information, the experimental results for the samples substituted with CN (sample **3**) and unsubstituted (sample **1**) were of reduced quality. As a result, some parameters in the Liptay formalism did not reliably

converge during Monte Carlo simulations. However, the results allowed for reliable qualitative interpretation that established revealing trends. The difference dipole moment determined for unsubstituted sample **1**, which was fitted with a value of $22 \text{ D} \pm 1$ because of the dominance of the linear Stark effect. We note that the TD-DFT calculations also predicted a slightly larger difference dipole moment when compared to the Br-substituted sample **2** (Table 2). The contribution from the positive first-order derivative line shape (positive α) to the Stark fit of the HOMO–LUMO transition increased through the series from sample **1** to sample **3** (see Supporting Information Table S3 and Figures S10–S12). The trend correlates with an increased delocalization of the LUMO because of substitution of the acceptor moiety. As for the parameter ζ , the fit to sample **3** proved to be very susceptible in terms of an initial guess for ζ but tended toward more consistent convergence of Monte Carlo simulations for smaller ζ values. In the case of sample **1**, the error margin for the ζ parameter is also large, but given the very similar experimental conditions to those for sample **2** (incidence angle = 37°) and the clearly reduced dichroic difference (Supporting Information), it can be safely deduced that the value for ζ is larger for sample **1** than for **2** and **3**. However, this may be exaggerated by the HOMO–LUMO transition overlap with higher lying transitions that may contaminate the fit. However, the fitting of the experimental data reflected the trend of decreased ζ with increased electron affinity of BTB.¹⁵ The greater the acceptor strength that is manipulated by group substitution, the more the CT nature of the transition becomes evident. The evidence suggests that this is chiefly due to a reduced bend angle between two 1,3-dithiole rings in the molecular geometry. We note the correlation between the calculated bend angle and the experimental ζ parameter through the series of samples. The discrepancy between the orientation of the transition dipole moment and difference dipole vectors in the experiments is reduced with reduced bend angle. This suggests that a greater bend angle that can be tuned by group substitution results in (i) greater sensitivity to solvent-induced fluctuations in the molecular geometry and/or (ii) a transition to an upper level that is more D⁺A (donor-localized) and D⁺A[−] (CT) than pure D⁺A[−]. Indeed, the gas phase computational results seem to account for the latter in which both the angles that m (transition dipole moment) and μ form with the long molecular axis tend toward smaller angles for sample **3** and slightly larger angles for sample **1**.

Insights into the Solvent Effect from DFT Calculations.

Taking what we have learnt from gas-phase DFT calculations and Stark spectroscopy into account, we tried to model accurately the effect of the solvent toluene in DFT calculations. By using the PBE0 functionals and PCM, the calculations predicted an increased dipole change over the $S_0 \rightarrow S_1$ transition for all samples. This resulted in better agreement with experimental results by 2–3 D. This, however, did not significantly influence the predicted polarizability change. We noted that the improvement was mainly due to the inclusion of solvent effects and that the relaxed geometry for toluene was very similar to the gas phase geometry. A limitation of the model may have been the absence of short-range solute–solvent interactions such as those referred to as π – π interactions³⁶ in the theoretical treatment. By forcing a change in the geometry around the bend angle, we see in Figure 3 that a larger bend angle results in an increased transition energy, an increased dipole moment change, and an increased polarizability change over the HOMO–LUMO transition. Although this does not bring the DFT calculations into perfect agreement with the experimental

results, we believe the results establish a trend that is revealing. The implication is that the solvent interaction causes further bending of the average bend angle. This can explain the blue-shifted HOMO–LUMO absorption peak in toluene with respect to the gas phase calculations in Figure 4 and listed in Table 1. It also implies a higher dipole moment change and polarizability change than predicted by only considering the solvent effects in DFT calculations, which we interpret as contributing to the slight discrepancy between the predictions of the DFT model and experimental results.

CONCLUSIONS

As an overall assessment of the information from calculations and fits to the experimental data, we believe to have confirmed the CT nature of the HOMO–LUMO transition. The strategy of validating results from calculation with fits to the experimental data and vice versa and in making reasoned adjustments in a step-wise fashion to achieve converging results, proved critical in arriving at these conclusions. In summary, the calculations predicted a charge displacement along the long molecular axis due to CT from the TTF moiety to the BTM moiety, resulting in a difference in dipole moment on the order of 10 D (and up to 17 D if solvent effects are taken into account) roughly parallel to the long molecular axis and the transition dipole moment. The change in polarizability was predicted to be on the order of $10 \text{ \AA}^3$ for all samples. The most reliable fitting to experimental data was achieved for sample **2** which resulted from optimal experimental conditions and a low signal-to-noise ratio. The sample showed a dipole change of 19 D, an angle between dipole change and transition dipole of 23° , and an isotropic change in polarizability tensor of $200 \text{ \AA}^3$. This represents a slightly larger dipole change than predicted by DFT calculations, a departure from calculation by an order of magnitude in the case of polarizability, and a slightly larger angle between transition dipole and change in dipole than anticipated. Calculations were very useful in identifying the other optical transitions in the spectral observation window. These provided two higher lying transitions because of the $S_0 \rightarrow S_5$ and $S_0 \rightarrow S_9$ transition with similar oscillator strength to the HOMO–LUMO transition and a difference dipole moment of 10 and 3 D, respectively. After fitting algorithms were applied to the Stark results, the two remaining Stark-active transitions were found in the predicted spectral regions and returned difference dipole moments in excellent agreement with theory. Although parameters extracted from the data resulting from the other two samples were more problematic in assessing quantitatively, they served to confirm some general properties and trends in agreement with the calculations. In both cases, the change in dipole was found to be roughly 20 D, and the calculations also predicted marginal changes in the difference dipole moment because of substitution of the acceptor moiety. A larger contribution in the Stark signal due to polarizability difference was observed through the series from sample **1** to **3**, as the LUMO becomes more delocalized. The angle between transition dipole moment and difference dipole moment was reduced for sample **3** with greater acceptor strength of the BTM moiety and conversely larger for sample **1** with reduced acceptor strength. We showed that the bend angle plays an important role in this regard. Using the experimental results, we tried to assess the influence of the solvent toluene on the dielectric properties of the molecules. By using a PCM of solvation, we could significantly improve agreement in terms of dipole moment change by 2–3 D between theory and experiment. By altering the

geometry with the assumption that short-range solute–solvent interactions that are not included in the theoretical model cause a significant change in the average molecular geometry, we showed that a larger bend angle would result in three correlated effects for the HOMO–LUMO transition. These effects are an increased transition energy, increased dipole moment change, and increased polarizability change. The implication is that the solvent interaction causes a more crooked average geometry of the TTF–BTB backbone than the DFT calculations anticipate. In a broader context, it is remarkable how drastic differences in the physical properties occur for this class of compactly fused donor–acceptor molecules when compared to “conventional” π -conjugated systems. As a consequence, such fused D–A systems appear very promising in the field of molecular electronics, for instance, as components for organic field-effect transistors³⁷ or nonlinear optics. The study of their electronic tunability and CT characteristics is extremely valuable.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Chemical structures of TTF-BTD samples.

Figure 2.
Schematic of the Stark spectrometer.

Figure 3. Dependence of difference polarizability tensor trace (top), dipole moment change (middle), and transition energy (bottom) for the HOMO–LUMO transition on the bend angle for all samples.

Figure 4.
Ground-state absorption spectra of samples 1–3 in toluene at room temperature.

Figure 5.

Low-temperature extinction coefficient spectrum $\epsilon(\nu)$ of sample 2. The circles represent the datapoints and the solid line represents the total fit to the unperturbed ground-state spectrum with contributions from three optically active transitions represented by a dotted line with asterisk markers in the HOMO–LUMO region and with a dashed line and dash-dotted line for higher lying transitions. The residual as difference between fit and data is shown below the main plot.

Figure 6.

Stark spectra for 38° incidence angle and horizontal probe polarization (circles) and vertical probe polarization (black dots) and the respective fits to the data (solid line and dashed line). The y -axis shows the change in extinction coefficient $-\epsilon(\nu)$ scaled to a 1 MV/cm applied field. The residuals as the difference between fits and data are shown below the main plot with a solid line for horizontal probe polarization and a dotted line for vertical probe polarization.

Figure 7.

Stark data (circles) and fit (solid line) for horizontal probe polarization and contributions to fitted Stark spectrum of the HOMO–LUMO transition and its zeroth (dashes), first (dash-dotted line), and second (dotted line) order derivative lineform. The contribution from the other transitions can be seen in Figure 8.

Figure 8.

Stark data (circles) and fit (solid line) for horizontal probe polarization and contributions to fitted Stark spectrum of the zeroth (dashes), first (dash-dotted line), and second (dotted line) order derivative lineform of the three optically active absorption transitions represented by red, green, and blue, respectively.

Table 1.

Energy, Wavelength, and Oscillator Strength of the HOMO–LUMO Transition for Each Sample Calculated by TD-DFT^a

$S_0 \rightarrow S_1$	E (eV)	λ (nm)	f	λ (nm) (exp.)
TTF–BTD _H (1)	2.403	516	0.2129	485
TTF–BTD _{Br} (2)	2.259	549	0.2303	515
TTF–BTD _{CN} (3)	1.846	672	0.2485	645

^aFor reference, the measured peak absorption wavelength for each sample at room temperature and with toluene as the solvent is included in the last column

Table 2.

Calculated Dipole Moment and Trace of Polarizability Tensor for the Ground and S_1 States as Well as the Associated Changes in the Dipole Moment and Trace of the Polarizability Tensor and the $S_0 \rightarrow S_1$ Transition Dipole Moment^a

	TTF-BTD_H (1)		TTF-BTD_{Br} (2)		TTF-BTD_{CN} (3)	
	S₀	S₁	S₀	S₁	S₀	S₁
μ_x (D)	1.059	0.334	1.118	0.579	1.034	0.935
μ_y (D)	1.064	14.962	1.410	14.381	3.608	13.337
μ_z (D)	0.000	-0.002	0.000	-0.002	0.000	-0.004
$ \mu $ (D)	1.501	14.965	1.799	14.393	3.753	13.369
$\text{Tr}(\alpha)$ ($\text{\AA}^3$)	141	159	163	170	170	153
	TTF-BTD_H (1)		TTF-BTD_{Br} (2)		TTF-BTD_{CN} (3)	
	S₀ $\rightarrow$ S₁		S₀ $\rightarrow$ S₁		S₀ $\rightarrow$ S₁	
$\text{Tr}(\alpha)$ ($\text{\AA}^3$)	18		7		-17	
$ \mu $ (D)	13.917		12.982		9.730	
m_x (D)	-0.2072		-0.1760		-0.1502	
m_y (D)	1.8902		2.0326		2.3391	
m_z (D)	0.000		0.000		0.000	

^aNote that the orientation of the coordinate axes may differ slightly for each sample and is shown in the Supporting Information (Figure S3)

Table 3.

Results of the Calculations Performed on 1–3 in Toluene Using the PCM of Solvation: Dipole Moment and Trace of the Polarizability Tensor in the S_0 and S_1 States and Associated Changes Upon the $S_0 \rightarrow S_1$ Transition

	TTF-BTD_H (1)		TTF-BTD_{Br} (2)		TTF-BTD_{CN} (3)	
	S₀	S₁	S₀	S₁	S₀	S₁
$ \mu $ (D)	1.673	18.266	2.059	17.829	4.602	16.201
$\text{Tr}(\alpha)$ ($\text{\AA}^3$)	170	196	197	209	211	186
	TTF-BTD_H (1)		TTF-BTD_{Br} (2)		TTF-BTD_{CN} (3)	
	S₀ $\rightarrow$ S₁		S₀ $\rightarrow$ S₁		S₀ $\rightarrow$ S₁	
$\text{Tr}(\alpha)$ ($\text{\AA}^3$)	26		12		-24	
$ \mu $ (D)	17.089		16.199		11.708	

Table 4.Extracted Parameters from Fits to the Experimental Data for Each Transition with $m > n > 1$

	μ (D)	ζ	$\text{Tr}(\alpha) (\text{\AA}^3)$	$m \cdot \alpha m (\text{\AA}^3)$
$S_0 \rightarrow S_1$	19 ± 1	$23^\circ \pm 6$	200 ± 50	120 ± 50
$S_0 \rightarrow S_n$	10 ± 2	$32^\circ \pm 10$	730 ± 150	530 ± 200
$S_0 \rightarrow S_m$	3 ± 1	N/A	180 ± 50	110 ± 50