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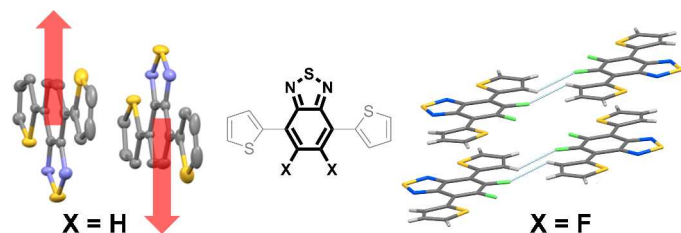


On the Effect of Fluorination of 2,1,3-Benzothiadiazole

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ABSTRACT: The 4,7-dithieno-2,1,3-benzothiadiazole (**DTBT**) moiety and its fluorinated counterpart are important π -conjugated building blocks in the field of organic electronics. Here we present a combined experimental and theoretical investigation into fundamental properties relating to these two molecular entities and discuss the potential impact on extended π -conjugated materials and their electronic properties. While the fluorinated derivative, in the solid state, packs with a smaller co-facial overlap than **DTBT**, we report experimental evidence for stronger optical absorption as well as stronger intra- and intermolecular contacts upon fluorination.

Introduction

The highly electron-deficient 2,1,3-benzothiadiazole unit is one of the most popular building blocks in organic electronics. Especially when designing molecularly hybridized push-pull type materials, where the alternating arrangement of electron-rich and electron-deficient units along the π -conjugated backbone effectively controls the frontier molecular orbitals, 2,1,3-benzothiadiazole is often the electron-deficient unit of choice.¹⁻⁴ To further fine-tune the frontier molecular orbitals as well as other important materials parameters such as solubility and crystallinity, chemical modifications of the 2,1,3-

benzothiadiazole unit has attracted much interest.⁵⁻⁸ Particularly fluorination has been shown to be an effective way to lower the highest occupied molecular orbital (HOMO) and thus obtain a better performing material for organic photovoltaics due to an improved open-circuit voltage.⁹⁻¹¹

While the effect of fluorination on the frontier energy levels is well understood,^{9,11} experimental details on the underlying reasons for observed differences relating to solubility, crystallinity, charge carrier mobility and bulk heterojunction blend morphologies with fullerene acceptors are lacking. Here, we compare the two well-known chromophores 4,7-dithieno-2,1,3-benzothiadiazole (**DTBT**) and its fluorinated derivative, 5,6-difluoro-4,7-dithieno-2,1,3-benzothiadiazole (**DTF2BT**) depicted in Figure 1. The detailed study of these two simple model compounds, which are frequently occurring building blocks in numerous high-performing organic electronic materials, highlights some important changes in physical properties upon fluorination.

Results and Discussion

DTBT and **DTF2BT** were synthesized according to literature procedures and single crystals were obtained from slow evaporation of hexane and toluene solutions, respectively. As shown in Figure 1, three coplanar conformations exist for the two chromophores. In the obtained crystals, both **DTBT** and **DTF2BT** show a strong preference for the **trans-cis** conformer as illustrated in Figure 2.

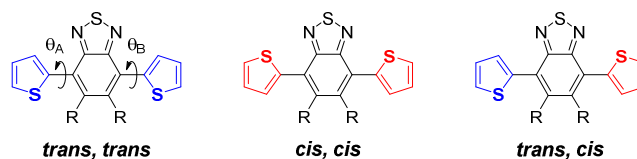


Figure 1. The molecular structures of **DTBT** (R=H) and **DTF2BT** (R=F) with different coplanar geometries defined by the dihedral (torsional) angles θ_A and θ_B .

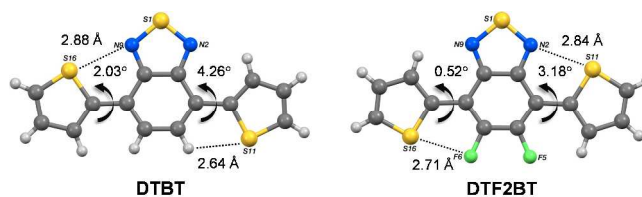


Figure 2. Crystal structures of **DTBT** and **DTF2BT** with major occupancy orientations displayed, see supporting information for the minor occupancy orientations.

Both crystal structures are disordered though. In the **DTBT** crystal, approximately 71% of the molecules are in the **trans-cis** conformation, while the remaining molecules adopt the **cis-cis** conformation. The **DTF2BT** crystal, meanwhile, shows minor occupancies of both the **trans-trans** (ca. 10%) and the **cis-cis** (ca. 27%) conformation. For **trans-cis DTBT**, the dihedral angles, θ_A and θ_B , are 2.03° and 4.26° , while a slightly higher degree of coplanarity is observed for **trans-cis DTF2BT** with dihedral angles of 0.52° and 3.18° as illustrated in Figure 2. The increased coplanarity of **DTF2BT** is reflected in short intramolecular contacts; especially the S-F and S-N distances (2.71 \AA and 2.84 \AA , respectively) are significantly shorter than the sum of the van der Waal radii. For comparison, the S-H and S-N intramolecular distances are 2.64 \AA and 2.88 \AA , respectively, in **DTBT**. Although the thiophenes are obviously disordered in both crystals, the stronger relative representation of the trans-conformation in the **DTF2BT** crystal as well as the higher degree of coplanarity and the short intramolecular S-F contacts are all indications of a planarizing effect from the fluorination of benzothiadiazole.

In contrast to the single crystal structures, quantum mechanical calculations using Gaussian at the B3LYP/6-31G* level of theory predict the **trans-trans** conformation to be most stable for both **DTBT** and **DTF2BT** with the **trans-cis** conformer being destabilized by 2.8 and 2.0 kJ mol^{-1} , respectively (Table S1). While the torsional degree of freedom has previously been studied theoretically for the two model compounds,¹¹ we used variable-temperature $^1\text{H-NMR}$ to investigate this aspect experimentally. Although the spectral line-broadening upon cooling (Figure 3) appears to be slightly more pronounced for **DTF2BT** than for **DTBT**, we were not able to reach the coalescence point neither in deuterated

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chloroform at 213 K nor in deuterated tetrahydrofuran at 183 K, where kT is on the order of 1.5 kJ mol^{-1} (Figure S1-S3). This indicates that the activation barrier for rotation (θ_A and θ_B) in solution is significantly smaller than what is predicted theoretically in vacuum.^{11,12}

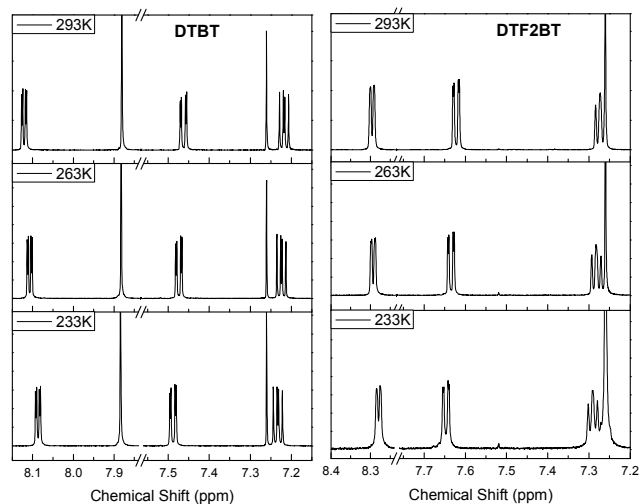


Figure 3. Aromatic region of $^1\text{H-NMR}$ spectra of **DTBT** (left) and **DTF2BT** (right) recorded in CDCl_3 at 293K, 263K and 233K.

UV-Vis spectroscopy was used to investigate the optical properties of **DTBT** and **DTF2BT** in solution as illustrated in Figure 4 and summarized in Table 1. Both model compounds show two absorption bands around 300 nm and 400-450 nm. While the high-energy absorption band coincides for the two compounds and is unaffected by changes in solvent polarity, the low-energy absorption feature is red-shifted approximately 20 nm for **DTBT** compared to **DTF2BT**. Moreover, **DTF2BT** shows a stronger solvatochromic effect with a 10 nm blue-shift when going from *n*-hexane to acetonitrile. We also note that the molar extinction coefficient (at both absorption features, Table 1) is consistently higher for **DTF2BT** than for **DTBT**, which of course is of paramount importance when considering these materials for organic photovoltaic applications.⁸

Quantum mechanical calculations were again used to support the experimental details and as depicted in Table 1, there is a fairly good agreement between the experimental and theoretical optical properties. The optical transition around 300 nm is predominantly from the HOMO to LUMO+1 transition and has

π - π^* character, while the lower energy feature is dominated by the HOMO to LUMO transition with strong intramolecular charge transfer (ICT) character. This also explains why the solvatochromism is only observed for the low-energy absorption band.

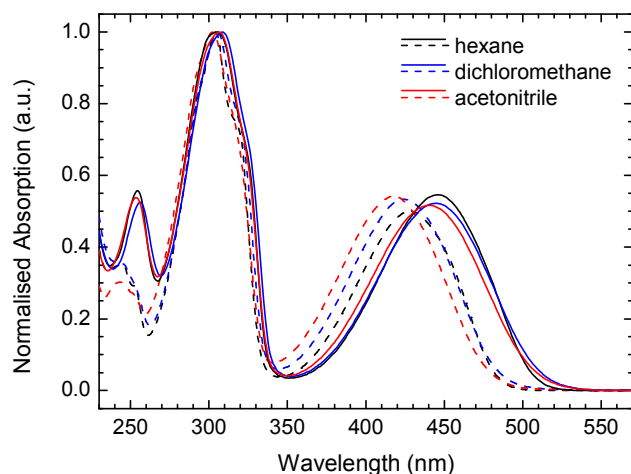


Figure 4. Normalised UV-vis spectra of **DTBT** (solid lines) and **DTF2BT** (dashed lines) in hexane (black), dichloromethane (blue) and acetonitrile (red) solution.

Turning our attention to the crystal packing of **DTBT** and **DTF2BT** (Figure 5 and Table 2), we note that **DTBT** is an orthorhombic crystal, while **DTF2BT** is distorted to a monoclinic crystal system with a β -angle of 104.82° . Viewing the two crystals along their a-axes reveal that both pack in a herringbone-type arrangement as often seem for small π -conjugated molecules.¹³ As illustrated in Figure 5C, the interplanar distances (d_2) between adjacent molecules are nearly identical for the two structures with values of 3.41-3.44 Å for **DTBT** and 3.44-3.46 Å for **DTF2BT**. The slipping distances (d_1) are slightly larger for **DTF2BT** (0.94-0.95 Å) than for **DTBT** (0.75-0.79 Å), which could potentially affect the charge transport in **DTF2BT** based materials adversely.^{14,15}

Table 1. Experimental and Theoretical Optical Properties of DTBT and DTF2BT in Solution

	solvent	λ_{\max} (nm)	ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{\max} (nm)	oscillator strength
		experimental	experimental	theoretical ^a	theoretical ^a
DTBT	<i>n</i> -hexane	306, 446	28.5, 15.5	325, 531	0.663, 0.364
	dichloromethane	309, 445	28.9, 15.2	325, 531	0.638, 0.371
	acetonitrile	306, 441	28.8, 14.9	325, 529	0.639, 0.357
DTF2BT	<i>n</i> -hexane	304, 428	33.4, 16.7	323, 518	0.771, 0.367
	dichloromethane	306, 424	31.0, 16.5	323, 513	0.753, 0.386
	acetonitrile	302, 418	29.2, 15.8	322, 510	0.741, 0.375

^aDetermined using Gaussian at the B3LYP/6-31G* level of theory.

Table 2. Crystal System, Space Group and Lattice Parameters for DTBT and DTF2BT Crystals

	DTBT	DTF2BT
Crystal System	orthorhombic	monoclinic
Space Group	Pbca	P2 ₁ /c
a, b, c [Å]	12.73, 9.88, 20.05	15.73, 4.81, 17.75
α , β , γ [°]	90, 90, 90	90, 104.82, 90

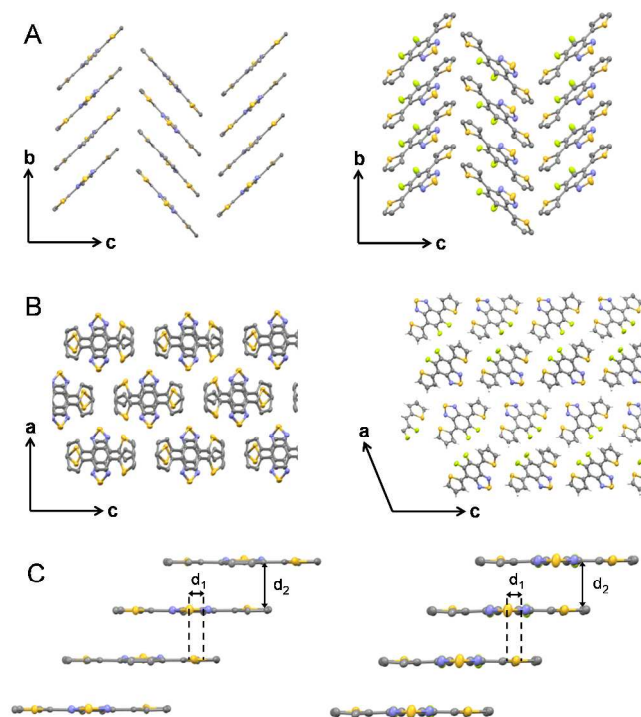


Figure 5. Crystal packing of **DTBT** (left pane) and **DTF2BT** (right pane) viewed along the a-axis (A), b-axis (B) and showing the slipping distance (d_1) and the interplanar distance (d_2) (C).

Calculated permanent dipole moments for the three different coplanar conformations for both molecules are depicted in Figure 6. The major occupancy **trans-cis** conformations have dipole moments of 1.18 D (**DTBT**) and 0.70 D (**DTF2BT**). Importantly, for **DTBT** the dipole moment is directed away from the electron-deficient thiadiazole ring, while the dipole moment of **DTF2BT**, due to its highly electron-withdrawing fluorine substituents, is directed towards the thiadiazole ring as illustrated in Figure 6. For **DTBT**, the other conformation present in the crystal (**cis-cis**) has an even stronger dipole moment of 2.21 D in the same direction, while the two minor conformations of **DTF2BT** have oppositely directed dipole moments.¹⁶

We believe that the large dipole moment of **DTBT** and the resulting strong dipole-dipole interactions are responsible for the antiparallel alignment of adjacent **DTBT** molecules depicted in Figure 6B. **DTF2BT**, on the other hand, has a much smaller permanent dipole moment and adjacent molecules are consequently observed to align in a parallel fashion along the π -stacking direction (Figure 6B). The change in direction of the dipole moment for **DTF2BT** with different conformations could potentially

account for some stabilizing dipole-dipole interactions in the crystal, but we find it unlikely to be the major driving force for this parallel packing. Instead, we note that adjacent π -stacks of **DTF2BT** have particularly close H-F contacts (2.51 Å) as illustrated in Figure 6C. Each **DTF2BT** molecule partakes in two intermolecular H-F interactions, while no similar intermolecular interactions could be observed for **DTBT**. Although we believe that these observations are the major factors governing the molecular packing motifs of **DTBT** and **DTF2BT**, it is worth noting that there are other potential intermolecular interactions that could affect the molecular packing.¹⁷

Taking into account the different conformations and their different permanent dipole moments, it is worth noting that the polarity of the solvent used during solution processing of **DTBT** and **DTF2BT** containing materials is likely to affect the distribution of conformations and thus also the solid state packing.¹⁶ In that context it is also worth noting that the two crystal structures are obtained from solvents with slightly different polarities.

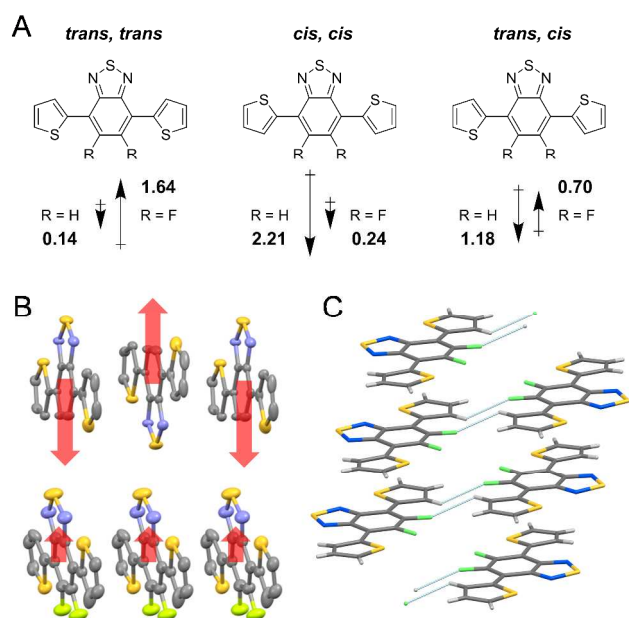


Figure 6. Calculated dipole moments for the three coplanar conformations of **DTBT** and **DTF2BT** (A), the alignment of dipole moments in the π -stacking direction (B), and intermolecular H-F interactions in the **DTF2BT** crystal (C).

The thermal properties of **DTBT** and **DTF2BT** were investigated with differential scanning calorimetry (DSC). In both cases only one phase transition from solid to isotropic melt was observed in the temperature range of 0-300 °C as illustrated in Figure 7. **DTBT** has a melting point of 119.9 °C with an enthalpy of melting of 23.0 kJ/mol, while **DTF2BT** melts at 213.6 °C with an enthalpy of melting of 25.8 kJ/mol. As the two chromophores have similar molecular symmetry and comparable conformational disorder in terms of cis/trans isomerism, the much higher melting point of **DTF2BT** compared to **DTBT** is most likely to stem from stronger intermolecular forces in the case of **DTF2BT**. This is in good agreement with the sharper crystallization peak for **DTF2BT** upon cooling as well as the crystal packing discussed above. Although **DTBT** shows intermolecular dipole-dipole interactions, these are likely weak due to the slip-stacked nature of the packing with each 2,1,3-benzothiadiazole unit interacting with neighboring thiophene units rather than neighboring 2,1,3-benzothiadiazole units as evident from Figure 5C. **DTF2BT**, on the other hand, shows strong intermolecular H-F interactions as well as intramolecular S-F and S-N interactions that help to minimize conformational disorder; interactions which are likely to be greatly contributing factors to the stronger crystal lattice of **DTF2BT**.

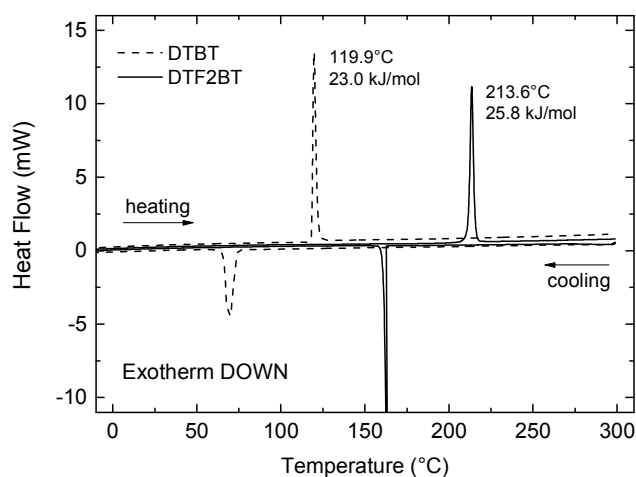


Figure 7. DSC traces of **DTBT** (dashed line) and **DTF2BT** (solid line) recorded at 10°C min⁻¹ under nitrogen.

Conclusions

1 In summary, to unambiguously compare the important chromophores **DTBT** and **DTF2BT**, a task
2 which is often obscured by other parameters such as molecular weight differences and solubility issues
3 when comparing the corresponding polymers, their crystal structures were solved and thoroughly ana-
4 lyzed in this contribution. This data was supported by ¹H-NMR, UV-Vis and DSC data as well as quan-
5 tum mechanical calculations. While **DTBT** packs with a slightly better co-facial overlap, **DTF2BT**
6 shows more prominent intra- and intermolecular interactions, which can be particularly important for
7 long-range charge transport in organic electronic materials. ¹H-NMR studies furthermore indicated that
8 the flanking thiophene groups can rotate freely even at low temperatures, which is in agreement with the
9 conformational disorder observed for both structures in the solid state. UV-vis spectroscopy showed that
10 **DTF2BT** is slightly blue-shifted and has a higher molar absorptivity than **DTBT**, which is of obvious
11 importance for photovoltaic applications. **DTBT** has a significantly larger permanent dipole moment
12 than **DTF2BT**, which affects the solid state packing and is also thought to affect the distribution of con-
13 formational orientations in solutions of varying polarity.
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31 ASSOCIATED CONTENT

32 Supporting Information

33 Additional information on the single crystal structures, the variable temperature ¹H-NMR studies and
34 the Gaussian-calculated energies of the molecular conformations of **DTBT** and **DTF2BT**. This material
35 is available free of charge via the Internet at <http://pubs.acs.org>.
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