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ABSTRACT

In this work, we study the light absorption properties of different novel molecules based on benzo[1,2-b:4,5-b']dithiophene (BDT), namely, BT-2F, BTRCl, and BTTzR, which hold great promise as electron-donor materials in organic solar cells. By employing density functional theory, we study the electronic states and related transitions in these systems. Moreover, in the case of BTTzR, we observe that the addition of two and three oligothiophene chains to the central benzene ring of the BDT unit leads to both a red-shift of the existing peaks and, interestingly, the development of new blue-shifted features, an effect that permits to enhance the panchromaticity of the molecule in the visible spectral range, thus rendering these new derivatives highly appealing as light absorbers in organic solar cells.

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INTRODUCTION

Together with other materials exhibiting high photovoltaic ability, such as metal-halide perovskites,¹⁻⁵ semiconducting polymers,^{6,7} quantum dots,^{8,9} and carbon nanotubes,^{10,11} small molecules are widely studied in the solar cell research community. In this regard, atomically precise synthesis of small-molecules allows a negligible batch-to-batch variation,¹² which is an important requirement for reproducibility and reliability of devices. For instance, fullerene derivatives have represented the workhorse electron-acceptor materials for decades,¹³⁻¹⁵ together with poly(thiophene) derivatives as electron-donor systems.^{16,17} However, fullerenes suffer from two important drawbacks: a relatively low absorption in the visible spectrum and photo-instabilities (i.e., dimerization); these considerably limit the power conversion efficiency (PCE) of the related devices.¹⁸

Therefore, recently, many reports have focused on the replacement of fullerene derivatives as electron-acceptor molecules in organic solar cells.¹⁹ For example, newly developed molecules such as BTPPT-4F (also called Y6) permit to achieve a noteworthy

efficiency of 16.02%.²⁰⁻²² In addition, the research of new donor materials has been fruitful in recent years. For instance, new and promising electron-acceptor molecules are based on the benzo[1,2-b:4,5-b']dithiophene (BDT) unit, as, for example, has been demonstrated in 2012 by Zhou *et al.*²³ Here, the authors reported excellent photovoltaic performance and power conversion efficiency as high as 7.38% (certified 7.10%) under AM 1.5G irradiation (100 mW cm⁻²). They attributed the excellent photovoltaic performance to the high mobilities and broadband absorption with relatively high oscillator strength owing to the efficient conjugation in the backbone structure and intramolecular charge transfer (ICT) between the terminal acceptor units (octyl cyanoacetate and 3-ethylrhodanine) and the central donor building block (BDT). Following this seminal study, in 2020, a novel small molecule donor, BTTzR, was developed, and an all-small-molecule solar cell employing BTTzR as the electron-donor showed an impressive power conversion efficiency (PCE) of 13.9%.²⁴ Such a high-efficiency was achieved thanks to the strong absorption in the wavelength range of 400–650 nm, as well as a wide optical bandgap of 1.88 eV, a low-lying highest occupied molecular orbital (HOMO) energy level

of -5.58 eV, and an ordered molecular orientation and packing. These results demonstrate that panchromaticity, i.e., the capability to absorb light in the whole visible range, is one of the key parameters necessary to achieve high PCEs.

Given the high interest in these promising functional materials, here, we analyze the light absorption features of different donor molecules, namely, BT-2F, BTRCl, and BTTzR. In the case of BTTzR, we study the electronic states and related transitions for BTTzR and its extended derivatives by means of density functional theory. By increasing the length of the thiophene pendants attached to the benzo[1,2-b:4,5-b']dithiophene (BDT) central unit of the molecule, we observe a red-shift of the absorption together with the development of new absorption features at higher energy. This aspect can be important to attain panchromaticity and thus to boost the photovoltaic efficiency of the related devices.

METHODS

The molecules have been designed with the Avogadro package.²⁵ We have optimized the geometries and calculated the electronic transitions by means of the density functional theory, with the ORCA package developed by Neese.²⁶ In these calculations, we have used the B3LYP functional.²⁷ Moreover, we have employed the Ahlrichs split valence basis set²⁸ together with the all-electron non-relativistic basis set SVPalls1.^{29,30} Finally, for these calculations, we have used the Libint library³¹ and the Libxc library.^{32,33}

RESULTS AND DISCUSSION

We have calculated the absorption spectrum of BDT, of BDT that are functionalized with two thiophene groups (T-BDT-T), and of BDT with four thiophene groups. The spectra are shown in Fig. 1(a). Indeed, we observe a clear red shift in the absorption and an

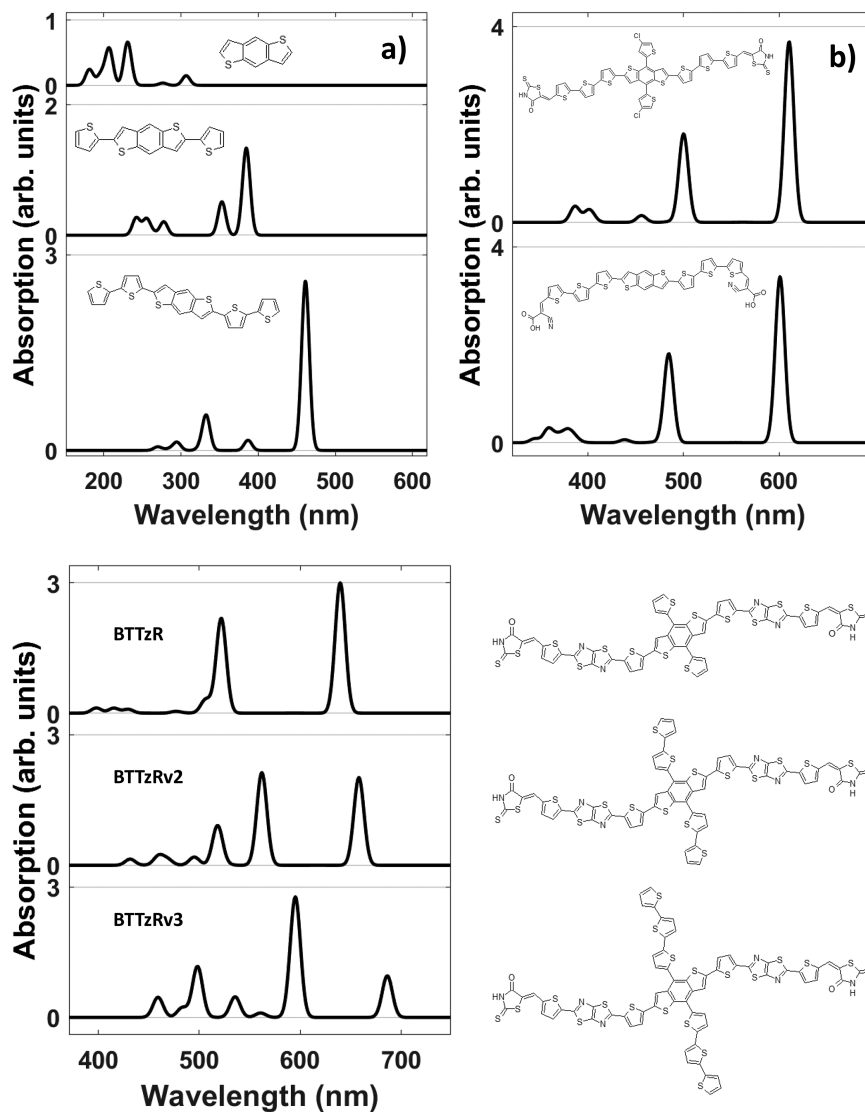


FIG. 1. (a) Calculated absorption spectra of benzo[1,2-b:4,5-b']dithiophene (BDT, top), of BDT functionalized with two thiophene groups (T-BDT-T, center), and of BDT functionalized with four thiophene groups (bottom). (b) Calculated absorption spectra of BTR-Cl (top) and BT-2F (bottom).

FIG. 2. (Left) Calculated absorption spectra for the molecules of BTTzR, BTTzRv2, and BTTzRv3. (Right) Sketches of the molecules.

increase in the oscillator strength, thanks to the conjugation length expansion because of the thiophene ring functionalization. We show the calculated absorption spectrum of BTR-Cl (top) and the spectrum of BT-2F (bottom) in Fig. 1(b). The lowest transitions are in good agreement with experimental data of these molecules.^{34,35} The two molecules are interesting since the solar cells employing these materials reach an efficiency of over 14% for BT-2F³⁴ and over 15% for BTR-Cl.³⁵

We have calculated the absorption spectra of BTTzR and BTTzRv2 (where _v2 is used to simply highlight that it is a second derivative/version of the molecule) with two thiophene molecules attached to the BDT unit and of BTTzRv3 in which three thiophene molecules are attached to the BDT unit. Such spectra are shown in Fig. 2. By increasing the number of thiophene molecules in the two pendants, we observe an increasing red shift of the electronic transitions. In particular, the red shift of the lowest electronic transition is clearly detectable. Moreover, the longer thiophene pendants are also related to a larger number of absorption peaks, with a significant oscillator strength (reported as *fosc* in the tables in the supplementary material), of the molecules.

By studying the optimized geometry of the BTTzR molecule, we have observed that the dihedral angle between the

thiazolo-[5,4-d]thiazole (TTz) group and the BDT group along the backbone of the molecule is 14° on one side and 3° on the other (Fig. 3). The dihedral angle between the thiophene molecule and BDT is 52° on one side and 55° on the other. These angles are in good agreement with the optimized geometries reported in the literature.²⁴

We have also studied the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of BTTzR, BTTzRv2, and BTTzRv3, highlighting that such orbitals (reported in Fig. 3), in particular the HOMO orbital, are significantly delocalized over the oligothiophene pendants in BTTzRv3. This leads to low-lying HOMO energy levels. In Fig. 3 (bottom left), we show the energy levels of BTTzR, highlighting the ground state at -5.41 eV and the four lowest singlet excited states at -3.25 , -3.17 , -2.69 , and -2.36 eV. We also show the four lowest triplet excited states at -3.92 , -3.87 , -3.65 , and -3.43 eV.

We show the energy levels of BTTzRv2 in Fig. 3 (bottom center). The ground state is at -5.36 eV, and the lowest four singlet excited states are at -3.25 , -3.17 , -2.71 , and -2.36 eV. With respect to BTTzR, we notice a ground state higher in energy. The lowest four triplet excited states are at -3.88 , -3.81 , -3.63 , and -3.40 eV. Finally, in Fig. 3 (bottom right), the energy levels of BTTzRv3 are

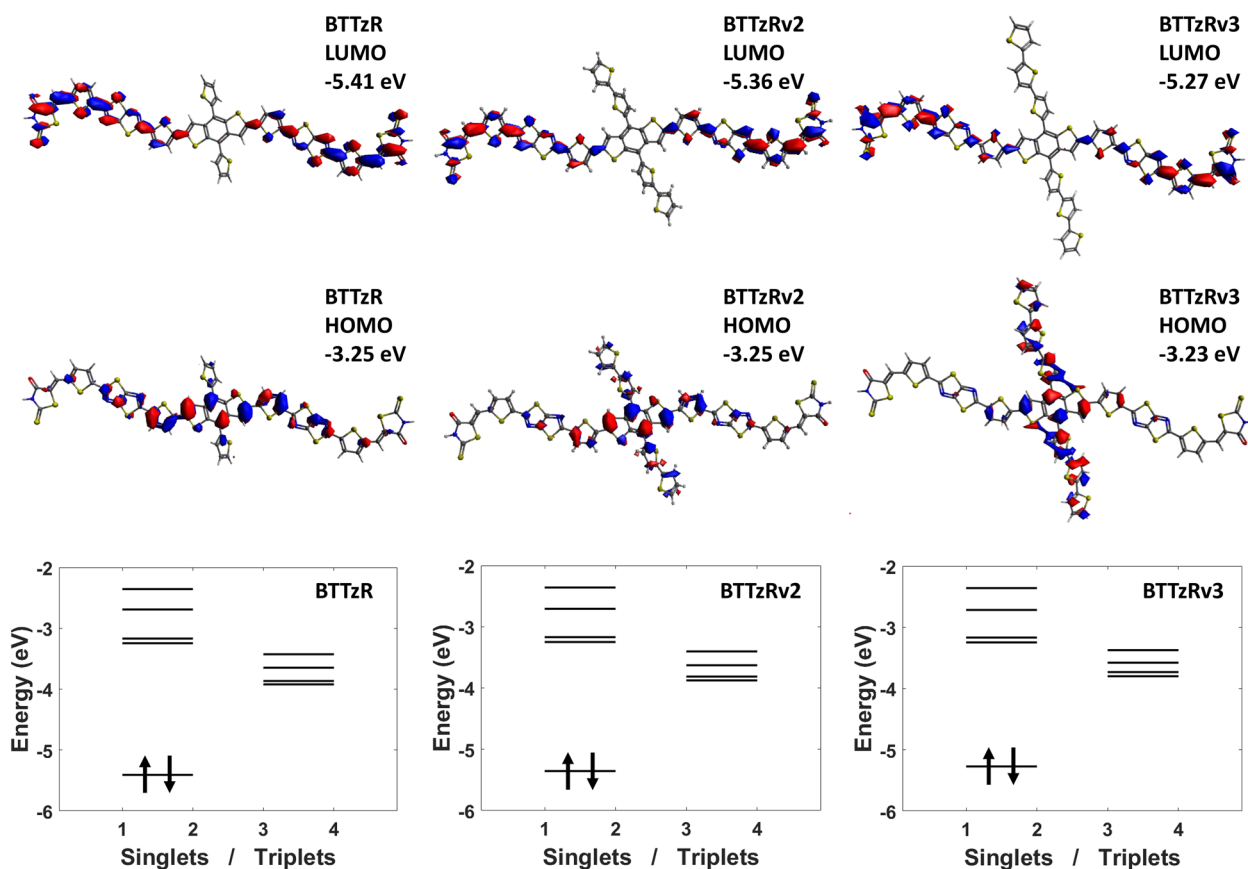


FIG. 3. Highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) for the BTTzR, BTTzRv2, and BTTzRv3 molecules. Bottom: Energy levels of BTTzR, BTTzRv2, and BTTzRv3 with the lowest four singlet excited states and the lowest four triplet excited states.

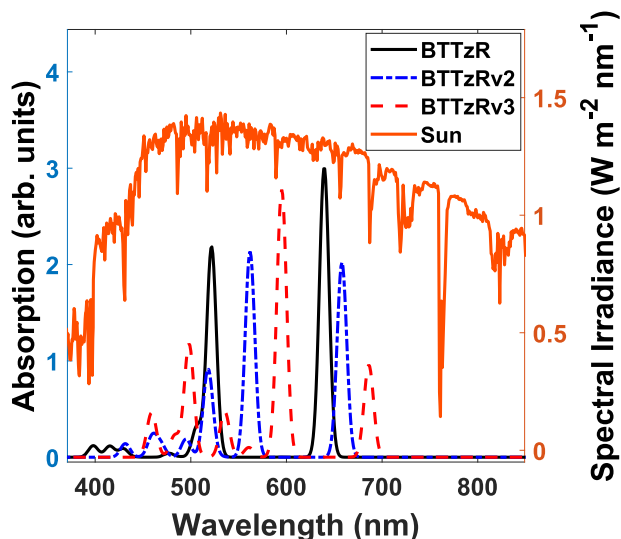


FIG. 4. Absorption spectra in the visible spectral range of BTTzR (solid black curve), of BTTzRv2 (dotted dashed blue curve), and of BTTzRv3 (dashed red curve). The direct and circumsolar irradiation of the Sun is given in dark orange.

depicted with the ground state at -5.27 eV (higher with respect to BTTzR and BTTzRv2), the lowest four singlet excited states at -3.23 , -3.17 , -2.71 , and -2.36 eV, and the lowest four triplet excited states at -3.80 , -3.73 , -3.58 , and -3.37 eV.

To remark the increasing panchromaticity by increasing the number of thiophene molecules in the pendants, we show in Fig. 4 the absorption spectra of BTTzR (solid black curve), BTTzRv2 (dotted dashed blue curve), and BTTzRv3 (dashed red curve) in the visible spectral range. The calculated lowest electronic transition is at lower energy with respect to the experimental one (in solution, it has been reported that the maximum absorption peak is at 528 nm),²⁴ and this could be due to a discrepancy between the dihedral angles in the calculated optimized geometry and the actual dihedral angles of the molecules in solution. Such discrepancy can be further studied in a future work by investigating the solvatochromism with the three molecules in different solvents. In the [supplementary material](#), we report the lowest 16 electronic (singlet to singlet) transitions and the lowest 16 triplets. Here, we notice a red shift of the lowest transition from BTTzR to BTTzRv2 and BTTzRv3 due to an increased delocalization, thanks to the longest thiophene chains attached to the BDT unit. Moreover, with BTTzR, we observe two intense absorption peaks, and with BTTzRv2, we observe three intense absorption peaks. Finally, with BTTzRv3, five intense absorption peaks at 685, 595, 535, 498, and 459 nm span a significant range of the visible spectrum. The larger number of absorption peaks of BTTzRv3 can lead to a potentially increased absorption of the Sun's irradiation (the orange curve in Fig. 4 displays the direct and circumsolar irradiation of the Sun, reference air mass of 1.5³⁶), useful for the fabrication of efficient photovoltaic cells. We also calculate the cation of BTTzRv3, and we report in the [supplementary material](#) the optimized geometry and the lowest 16 electronic transitions. We observe a remarkable red shift of the lowest electronic transitions in the cation with respect to the ones of the neutral molecules with transitions at about $2.4 \mu\text{m}$

with a non-negligible oscillator strength. This result is very interesting since it can shed light on the nature of the photo-ionized species of BTTzRv3 in a possible heterojunction with an acceptor material. Such a finding will be further studied in a future work.

CONCLUSION

In this work, we have studied the optical properties in the visible range of the donor molecule BTTzR and of two derivatives of BTTzR in which we have increased the number of thiophene molecules attached to the BDT central unit. We have calculated the singlet and triplet excited states, noticing a red-shift in such levels by increasing the number of thiophene molecules. Furthermore, addition of the thiophene pendants leads to the appearance of new blue-shifted absorption features, which could lead to increased panchromaticity and power conversion efficiencies in the related solar cells.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for electronic transitions and optimized geometries (xyz coordinates) of all the studied molecules.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors declare no potential conflicts of interest.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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