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Article

N-Annulation of the BTI Rylene Imide Organic Building Block: Impact on the Optoelectronic Properties of π -Extended Molecular Structures

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Abstract: Benzothioxanthene imide (BTI) has recently emerged as an interesting and promising block for organic electronics. In this contribution, we report on the impact of the *N*-annulation of the latter dye on the optoelectronic of π -extended molecular structures. To do so, the thiophene-diketopyrrolopyrrole was selected, as central π -conjugated core, and either end-capped with two BTIs or its *N*-annulated version, namely the TCI. While almost similar band gaps were measured for individual rylene imide dyes, significant differences were highlighted, and rationalized, on their π -extended counterparts.

Keywords: benzothioxanthene imide; thiochromenocarbazole imide; organic synthesis; Structure–property relationships; organic photovoltaics



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1. Introduction

Over the last decades, rylene-imide-based dyes have attracted considerable research attention [1–3]. Among them, the naphthalene [4–7] and perylene [8–11], functionalized by either one or two imide groups, have quickly emerged as key players in the landscape of organic semiconducting materials. Thanks to the creativity of chemists, a myriad of site-selective functionalizations have been reported, leading to the preparation and characterization of a significant number of new and original π -extended molecular and macromolecular systems [12]. Characterized by remarkable optoelectronic properties, high chemical/thermal stability, and a certain ease of synthesis, a good number of these structures have been successfully used in several devices including organic light emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic solar cells (OSCs) [1,13–18].

On the fringe of this success story, we have recently focused our attention on another member of this rylene family, namely the benzothioxanthene imide (BTI, Figure 1A). Ignored or simply unknown by the organic electronic community, this sulfur-containing structure was first reported in the early 70 s [19,20] and was mainly used as a fiber dyeing agent and fluorescent probe for bio-imaging [21–23]. In these early reports, it was functionalized solely for grafting and/or solubility reasons on the imide nitrogen atom, however, we have demonstrated the first selective halogenation(s) of its π -conjugated core [24,25]. Beyond the preparation of original π -extended/conjugated BTI-based architectures, this

new class of compounds was also successfully used as the active component in the above-mentioned devices, thus highlighting, for the first time, their promising potential of BTI in organic electronics [24,26–28].

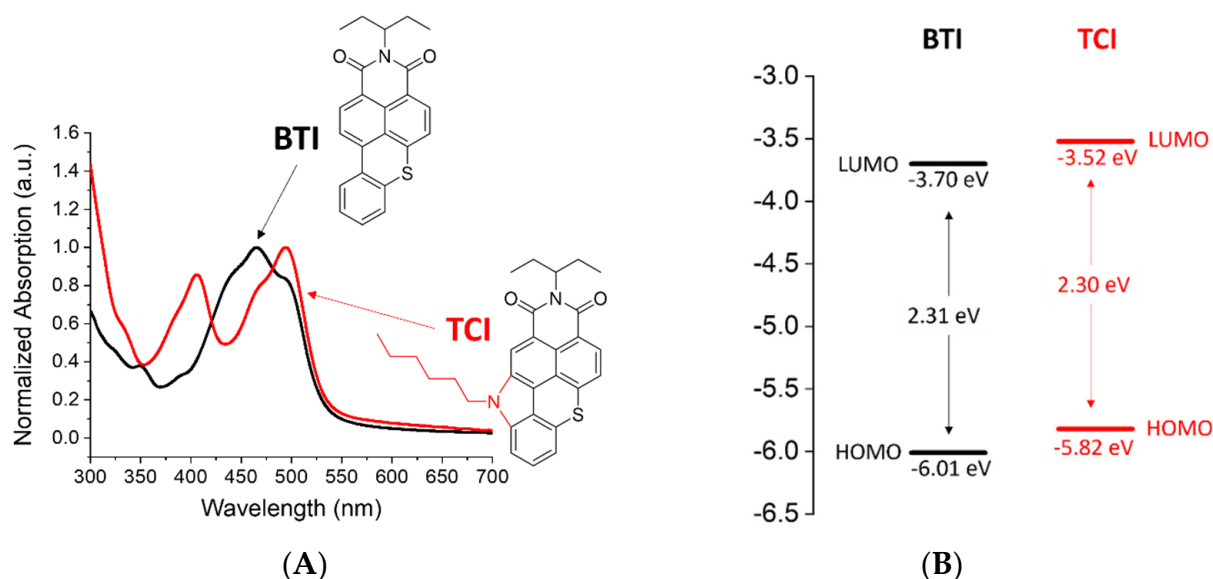


Figure 1. (A) Structures and solid state UV-visible spectra of BTI and TCI. (B) Frontier orbital energy diagram of both dyes in solid.

As a step forward in the chemical exploration of this dye, we lately achieved the *N*-annulation of its bay position, affording the thiochromenocarbazole imide, acronymed TCI (Figure 1A) [29]. Interestingly, incorporation of this fused, nitrogen-based 5-membered ring was found to induce a concomitant destabilization of both the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO), resulting in an almost similar band gap (2.31 eV vs. 2.30 eV, Figure 1B).

In this study, thiophene-diketopyrrolopyrrole was selected as a π -bridge for its (i) ease of synthesis [30], (ii) compatibility with direct (hetero)arylation cross coupling reactions [31,32] and (iii) absorption in the visible that would, we hoped, shift those of the target compounds into the far red or near-infrared regions; an electromagnetic range of interest in many optoelectronic and bio-related applications (Figure 2) [33–36]. For instance, this *rylene imide-DPP-rylene imide* scaffold has been used successfully to develop non-fullerene acceptors for organic solar cells [37–39].

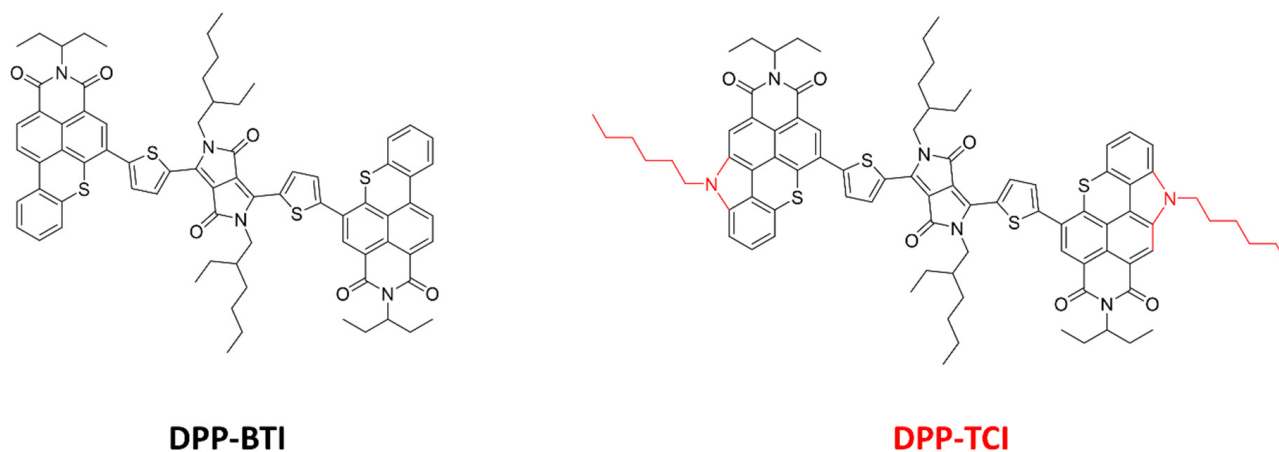
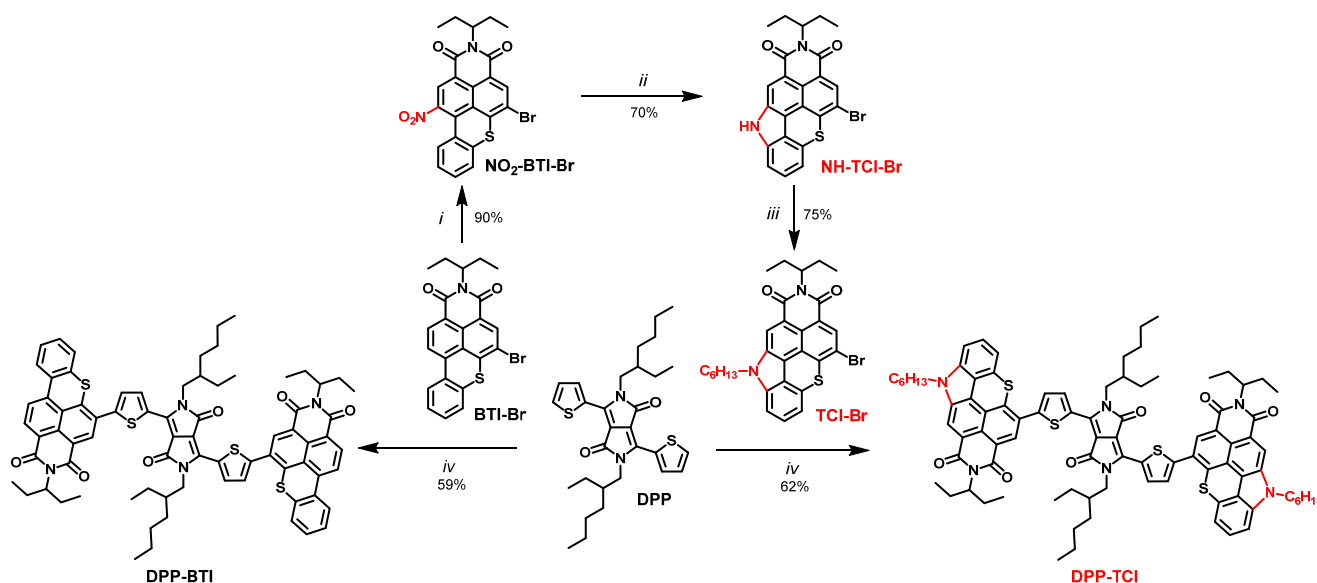


Figure 2. Structure of the two DPP based compounds studies in this contribution, namely DPP-BTI and DPP-TCI.

2. Results and Discussion

The synthetic route to the target compounds, namely **DPP-BTI** and **DPP-TCI**, is depicted in Scheme 1.



Scheme 1. Synthetic routes to **DPP-BTI** and **DPP-TCI**. (i) HNO_3 , CH_2Cl_2 , r.t. (ii) triphenylphosphine, DMF, reflux. (iii) K_2CO_3 , 1-bromohexane, DMF, $120\text{ }^\circ\text{C}$. (iv) SiliaCat[®] DPP-Pd, K_2CO_3 , PivOH, DMAc, $80\text{ }^\circ\text{C}$.

The materials were prepared following our previously reported procedure [24]; **BTI-Br** was selectively nitrated in its bay position prior to undergoing a Cadogan reductive cyclization reaction in presence of triphenylphosphine [29]. The resulting **NH-TCI-Br** was subsequently treated with 1-bromohexane under basic conditions to afford a *N*-alkylated and -annulated version of the **BTI-Br**, namely the **TCI-Br**. Both compounds were finally engaged in a heterogeneous palladium-catalyzed direct C-H arylation reaction with the DPP dye. Upon completion, both compounds were isolated from the crude by simple column chromatography on silica gel.

The molecules were found to be highly soluble in common organic solvents; their optical properties were first investigated in solution with comparison to their individual constituting building blocks, namely the **BTI**, **TCI** and **DPP** (Figure 3).

Interestingly, their characteristic absorption bands can be specifically attributed to the spectral features of their constituent π -extended molecules (**DPP-BTI** and **DPP-TCI**), even if shifted, to a greater or lesser extent, toward the longer wavelengths. Correlated to an improved donating effect, induced by the carbazole moiety, this redshift was indeed found to be more pronounced in the case of the **TCI**-based compound (**DPP-TCI**). Regarding the optical signatures of the rylenes, a 13 nm shift was indeed observed for both characteristic bands of the *N*-annulated **TCI** (ca. 400 and 470 centered bands) when coupled to the **DPP** central core while only ca. 3 nm were measured for its **BTI** counterpart. Furthermore, the most drastic difference was observed for the band at lower energies, attributed to the **DPP** core, with a 41 nm shift for the **DPP-TCI** molecule (λ_{max} from 548 nm to 589 nm) vs. ca. 28 nm for the **DPP-BTI** molecule (λ_{max} from 548 nm to 576 nm). As a result, with an onset at ca. 640 nm, **DPP-TCI** exhibits a reduced band gap of ca. 0.06 eV compared to its **BTI**-based parent compound ($\lambda_{\text{onset}} = 664\text{ nm}$). On the other hand both molecule shows fluorescent properties in the far red-region (Table 1, Figure S10). With similar quantum yields (of ca. 60%), emission band of **DPP-TCI** also appears slightly redshifted (of ca. 6 nm) compared to that of **DPP-BTI**.

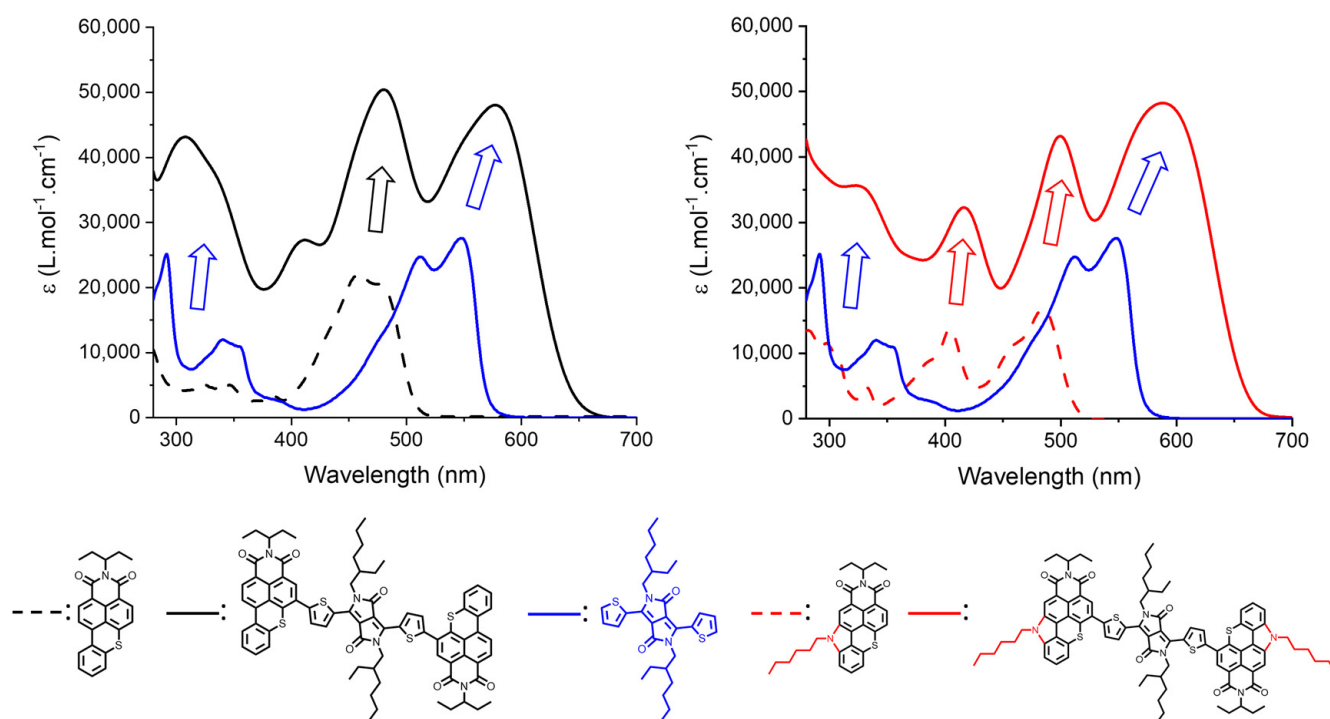


Figure 3. Comparison of the UV-visible spectra of **DPP-BTI** (black, full line) and **DPP-TCI** (red, full line) with their respective building blocks, i.e., the **BTI** (black, dash line), the **TCI** (red dash line) and the **DPP** (blue, full line) in CHCl_3 solution.

Table 1. Summary and comparison of the optical data of **DPP-BTI** and **DPP-TCI**.

Compound	λ_{max} Solution (nm)	ϵ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)	λ_{em} Solution (nm)	Q_f^a	λ_{max} Film (nm)	Onset Film (nm)	E_g^{opt} Film (eV)	HOMO (eV) ^b	LUMO (eV) ^c
DPP-BTI	577	48,000	655	0.62	601	708	1.75	−5.68	−3.93
	480	50,000			488				
	411	27,000			426				
	308	43,000			337				
DPP-TCI	588	48,000	661	0.60	616	733	1.69	−5.45	−3.76
	499	43,000			505				
	416	32,000			425				
	324	35,500			340				

^a Measured using Coumarin-153 as reference ($\Phi_f = 0.45$ in MeOH); ^b Determined by photoemission spectroscopy in air (PESA); ^c LUMO = (HOMO) − E_g^{opt} (film).

In the thin film state, absorption spectra broaden and redshift (due to solid state aggregation), thus leading to even more reduced band gaps while maintaining the same trends observed in solution (Figure 4a and Table 1).

The greater impact on the HOMO level can be attributed to the improved donor character of the **TCI** blocks induced by the alkylated nitrogen atom constituting the carbazole ring while a reduced gap can be attributed to better conjugation along the backbone. The shallower HOMO level of **DPP-TCI** was also highlighted by the photovoltaic parameters observed in organic solar cells prepared from both the **DPP** based compounds, used as molecular donors. To do so, direct solar cells of architecture: ITO/PEDOT:PSS/active layer/LiF/Al were fabricated and tested under AM 1.5 G conditions. Once blended with (6,6)-Phenyl C_{71} butyric acid methyl ester (PC_{71}BM) best power conversion efficiencies were achieved in an optimal 1 to 3 weight to weight donor: acceptor ratio. As depicted in the respective current-to-tension (J-V) curves, plotted in Figure 5, higher open circuit voltage (V_{oc}) values and therefore efficiencies were systematically achieved with the **DPP-BTI** than **DPP-TCI**. (Table 2).

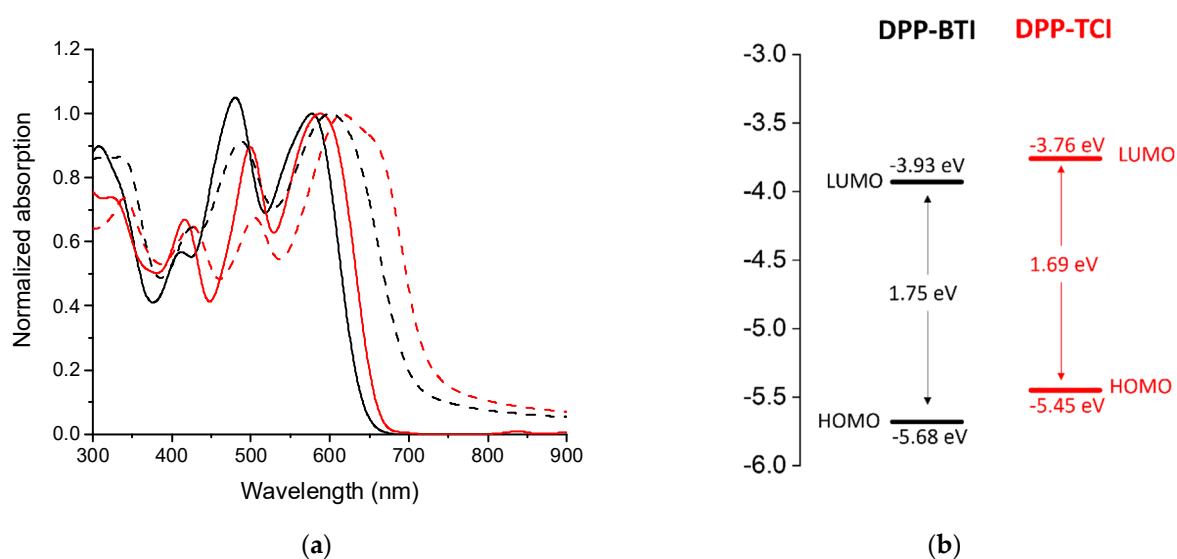


Figure 4. (a) Comparison of absorption spectra in solution (full line) and solid state (dash line) of **DPP-BTI** (black) and **DPP-TCI** (red). (b) Frontier orbital energy levels were estimated and compared, as shown in (b). The N-annulation of the **BTI** results in a concomitant destabilization (upward shift in energy) of both the HOMO ($\Delta_{\text{HOMO}} = 0.23$ eV) and LUMO ($\Delta_{\text{LUMO}} = 0.17$ eV) of the π -conjugated **DPP-TCI**, along with a reduction of the band gap ($\Delta_{\text{Eg}} = 0.06$ eV).

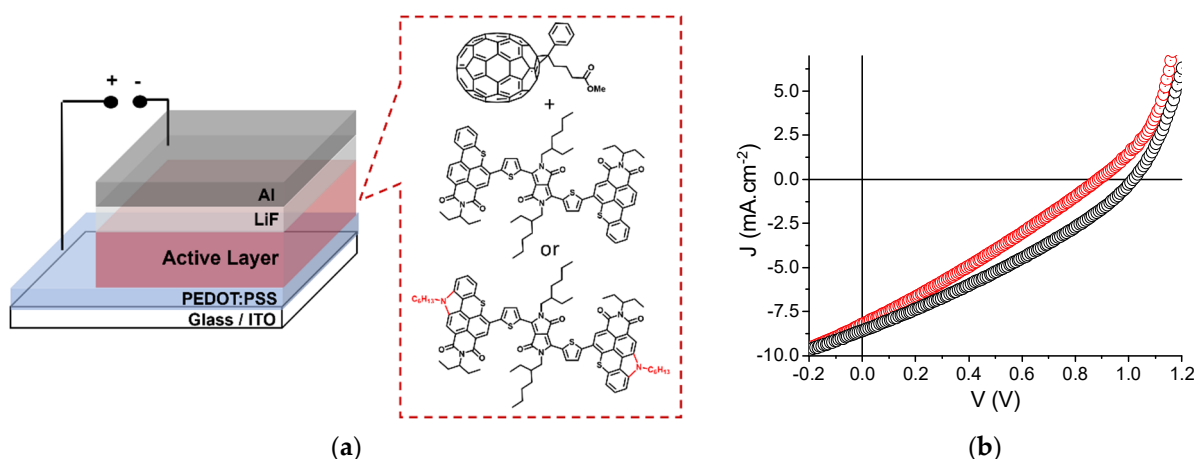


Figure 5. (a) Architecture of the organic solar cells used to evaluate the photovoltaic properties of **DPP-BTI** and **DPP-TCI**. (b) J-V curves of the best devices prepared either with **DPP-BTI** (black) and **DPP-TCI** (red) once blended with **PC₇₁BM** (in a 1:3 w:w donor:acceptor ratio).

Table 2. Best photovoltaic parameters (average values from 6 devices in brackets).

Compound	V_{oc} (V)	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	FF (%)	PCE (%)
DPP-BTI	1.02 (1.01 ± 0.02)	8.55 (8.49 ± 0.07)	31 (29 ± 2)	2.70 (2.48 ± 0.18)
DPP-TCI	0.88 (0.87 ± 0.01)	8.19 (8.15 ± 0.08)	28 (27 ± 1)	2.01 (1.93 ± 0.07)

It is indeed usually generally accepted that the latter parameter (V_{oc}) is proportional to the difference between the LUMO of the acceptor (fullerene) and the HOMO of the donor (rylene imide **DPP** based compound), consistent with the observed trend in energy levels [40].

In order to understand the electronic structure of the molecules, density functional theory (DFT) calculations were performed. Optimized geometries are shown in Figure 6a, while the torsion angle between DPP and BTI or TCI units (measured as the dihedral angle in the bonds between atoms 1, 2, 3 and 4, highlighted in green in Figure 6a) was calculated and revealed a larger torsion angle for DPP-BTI (61.85°) than for DPP-TCI (50.14°), as depicted in Figure 6b. DFT results show that adding the N-annulated 5-membered ring in DPP-TCI increases (i) the energy of both the HOMO and LUMO orbitals of the molecule relative to DPP-BTI, consistent with HOMO and LUMO energy levels determined experimentally by PESA and UV-vis, and (ii) the HOMO energy to a greater extent than the LUMO, resulting in the reduction of the band gap.

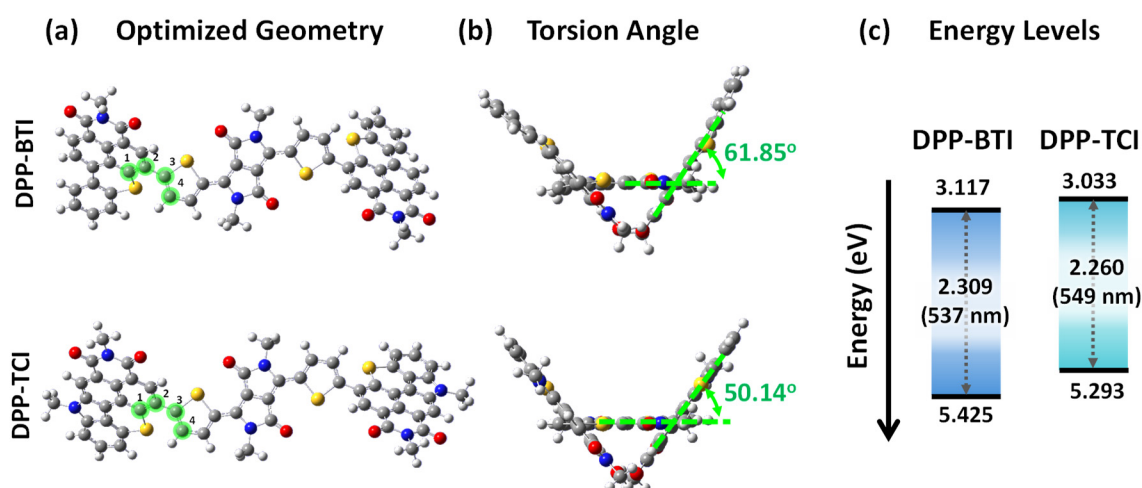


Figure 6. Optimized geometries of both DPP-BTI and DPP-TCI computed using the B3LYP density-functional treatment in the standard 6-311G basis set and values of the torsion angles measured between the rylenes and the thiophene connector.

This decreased band gap in DPP-TCI (2.260 eV) compared to 2.309 eV for DPP-BTI, corresponds to HOMO—LUMO transitions occurring at 537 nm or 549 nm for DPP-BTI or DPP-TCI, respectively (Figure 6c). These calculated values are somewhat blueshifted compared to the measured values in solution (577 and 588 nm, respectively) however, gas-phase DFT calculations are expected to be blue-shifted compared to condensed phases (solution or film) and the difference in absorption onset and optical band gap between the two chromophores is in excellent agreement with the experimentally observed value (12 nm calculated red-shift vs. 11 nm observed red-shift).

These differences can be attributed to the relatively stronger electron-donating character of the annulated N-atom compared to the two C-H bonds that it replaces in DPP-BTI. N-alkyl groups are indeed known to be strongly electron-donating, additionally, the N-containing 5 membered ring incorporates N as a subunit of larger pyrrole, indole or carbazole structures, all of which are known as relatively electron-rich/electron-donating sub-structures. The measured frontier orbital energies and decrease in bandgap confirm the electron-donating character of the appended N-annular ring.

On the other hand, the decrease in torsion angle between the DPP and TCI groups can be rationalized as being caused by an increase in bond order between DPP and TCI relative to DPP and BTI; in other words, more double-bond character, better p-orbital overlap, and increased π -conjugation exists in the DPP-TCI bond, which manifests as a smaller torsion angle. It has been shown by Marder et al., in push-pull type chromophores, the bond length alternation (BLA) is decreased when stronger electron donating or electron withdrawing groups are used, leading to improved quinoid contribution to the ground state and corresponding increase in bond order between coupled aromatic rings [41,42]. Both DPP-BTI and DPP-TCI can be considered push-pull chromophores, DPP being a relatively electron-withdrawing moiety, while TCI shows a stronger electron-donating

character compared to **BTI**. Hence, the increased electron-donating character of **TCI** results in more double bond character between **DPP** and **TCI** than between **DPP** and **BTI**, despite identical steric interactions near the bond linking the two groups. This interpretation is consistent with the observed shortening of the bond length in **DPP-TCI** (1.468 Å) compared to **DPP-BTI** (1.473 Å), as seen in the computed optimized geometries.

3. Conclusions

As part of our endeavor to fully explore the potential of **BTI**-based derivatives, we have thus investigated the impact of *N*-annulation on the properties of π -extended structures, since similar band gaps were observed for both rylene parent structures (**BTI** and its *N*-annulated version, **TCI**). Thus, two π -conjugated compounds, based on a common thiophene-diketopyrrolopyrrole central core and end-capped with each rylene imide, were prepared by direct arylation. We observed that incorporation of the nitrogen-containing 5-membered ring in the **TCI** structure resulted in increased donor character and improved electronic conjugation along the backbone, resulting in shallower frontier orbital energy levels and a concomitant reduction of the band gap (approaching the near-infrared region in this case). The reduced band gap and increased π -conjugation in the **DPP-TCI** structure were attributed to a decrease in bond length alternation and an increase in the order of the bond linking **DPP** to **TCI** relative to the **DPP-BTI** bond. Hence, we show that a simple Cadogan cyclization turns out to be an easy and accessible strategy to fine-tune the energetics of **BTI**-based extended molecules, while at the same time providing additional orthogonal reactive sites at the carbazole N-atom available for functionalization with a variety of lateral side chains/groups. This work opens the door for further customization of **BTI**-based molecules, which can be conveniently optimized as absorbers, emitters and transport materials for a variety of optical and optoelectronic applications.

Supplementary Materials: The following supporting information, including synthetic procedures [24,29,43], spectroscopic data, photovoltaic fabrication details and computational data [44–46], can be downloaded at: <https://www.mdpi.com/article/10.3390/colorants2010002/s1>.

Author Contributions: Organic synthesis: T.G., J.M.A.C., P.J., J.B. and Y.Z. Characterization and device fabrication: S.A. and G.C.W., computational chemistry: B.W., supervision of S.A., S.T., P.B., ideas and writing: P.J., B.W. and C.C. All authors have read and agreed to the published version of the manuscript.

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