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\(\alpha,\beta\)-Unsubstituted \textit{meso}-Positioning Thienyl BODIPY: A Promising Electron Deficient Building Block for the Development of Near Infrared (NIR) \(p\)-type Donor-Acceptor (D-A) Conjugated Polymers

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Abstract

It is demonstrated that $\alpha,\beta$-unsubstituted meso-positioning thienyl BODIPY is an electron deficient unit that leads to the development of ultra low optical band gap ($E_{g}^{\text{opt}} < 1$ eV) $\pi$-conjugated D-A quarterthiophene polymers. Furthermore, it is revealed that the optoelectronic, electrochemical and charge transporting properties of the resulting $\alpha,\beta$-unsubstituted meso-positioning thienyl BODIPY quarterthiophene-based polymers are alkyl side chain positioning dependent. Tail-to-tail (TT) positioning of the alkyl side chains at the two central thiophenes of the quarterthiophene segment results to lower $E_{g}^{\text{opt}}$, higher energy levels and increased hole mobility as compared to head-to-head (HH) positioning. Finally, even though the synthesized polymers exhibit high electron affinity, higher even to that of the fullerene derivative [6,6]-phenyl-C$_{71}$-butyric acid methyl ester (PC$_{71}$BM), they present only $p$-type behaviour in field effect transistors (FETs) independent to the alkyl side chain positioning.

Keywords: conjugated polymers, Near Infrared (NIR), BODIPY, dyes, polythiophenes

† Electronic supplementary information (ESI) available: Instrumentation, theoretical calculations, synthesis of monomers and polymers, $^1$H-, $^{13}$C- nuclear magnetic resonance (NMR) and mass spectroscopy of monomers, gel permeation chromatography (GPC) of polymers, absorption spectra of the monomers. Transport characteristics of the devices. See DOI: 10.1039/…………….
1. Introduction

Low-bandgap (LBG) semiconducting polymers with bandgaps smaller than 1.4 eV and absorption cut-off in the near infrared (NIR) are of great interest for organic photovoltaics (OPV), organic photodetectors (OPDs), ambipolar field-effect transistors (FETs) and bio-imaging applications.\textsuperscript{1-6} Intense efforts have been devoted to the synthesis of new LBG donor-acceptor (D-A) polymers for such applications, and noteworthy progress has been made.\textsuperscript{7-23} One of the most promising class of LBG $\pi$-conjugated D-A polymers are those consisting of quarterthiophene as the electron donating (D) unit with various electron deficient (A) units such as cyclopentadienone (1),\textsuperscript{7d} benzobisthiadiazole (2),\textsuperscript{7h} diketopyrrolopyrrole (3),\textsuperscript{8e-g} phenanthrene (4)\textsuperscript{15a} or benzodithiophene (5)\textsuperscript{15c} condensed thia dizoloquinoxaline, indeno[1,2-b]fluorene-6,12-dione (6),\textsuperscript{16c} 2,2$'$-(inden o[1,2-b]fluorene-6,12-diylidene) dimalononitrile (7),\textsuperscript{16c} bisindenofluorene-12,15-dione (8),\textsuperscript{16c} 2,2$'$-(bisindenofluorene-12,15-diylidene) dimalononitrile (9)\textsuperscript{16c,d} and fused aromatic thieno[3,4-b]pyrazine (10)\textsuperscript{22c} (Figure 1).

![Chemical Structures]

Fig. 1 General chemical structures of donor-acceptor (D-A) $\pi$-conjugated polymers containing quarterthiophene segments as the electron donating (D) units (in red) and various electron deficient (A) moieties (in blue).
Among the various electron deficient (A) building blocks, one of the less explored for the synthesis of LBG \( \pi \)-conjugated D-A polymers still remains the 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, commonly known as BODIPY (Figure 1).\(^{24,25}\) From the limited examples of \( \pi \)-conjugated polymers based on 1,3,5,7-tetramethyl substituted BODIPY,\(^{26-32}\) it is revealed that they can potentially extend the absorption into the deep-red regions of the visible spectrum and, in some cases, are excellent NIR emitters.\(^{25}\) However, the presence of the methyl substituents on BODIPY core can prevent the planarity of the polymer chains and as a consequence to inhibit the full exploitation of the optoelectronic properties.\(^{33}\) Lately, to avoid the steric effect of the methyl groups, \( \alpha,\beta \)-unsubstituted BODIPY moieties have been designed, synthesized and effectively integrated into the polymer backbone either through electropolymerization\(^{34,35}\) or metal catalysed cross coupling polymerization.\(^{36,37}\)

Another challenge in the chemical structure optimization of the quarterthiophene based-\( \pi \)-conjugated D-A polymers is the positioning and type (linear versus branched) of the alkyl side chains as can be seen in Figure 1. To cope with this challenge, often various alkyl side chains are screened and attached to the polymer backbone.\(^{38}\) Alkyl chains are the most commonly used side chains in polymeric semiconductors. Whereas their initial role was to ensure polymer solubility in organic solvents and good processability towards thin-film formation,\(^{39}\) today, more and more studies have demonstrated the substantial impact of the flexible chains on the supramolecular self-assembly through different intermolecular interactions of the polymer chains\(^{40,41}\) and consequently on their charge carrier transport properties and device performances. Even subtle changes of the flexible chains may greatly influence the device performance.\(^{42-44}\) Parameters that influence the molecular packing include the length of the side chains\(^{45,46}\) as well as the substitution position,\(^{43,47}\) their density\(^{48,49}\) and the bifurcation point of branched alkyl chains.\(^{42,50,51}\) The optimum choice of alkyl
side chains is not universal. For each semiconducting polymer, an extensive screening of structural modifications is required.

Recently, our group has demonstrated that aromatic cross-coupling polycondensation on 2,6-positions of an $\alpha,\beta$-unsubstituted BODIPY functionalized with thienyl group at the meso-position is possible, resulting to an ultra LBG (1.15 eV) $\pi$-conjugated polymer that was employed as electron donor material in NIR OPVs.\textsuperscript{37} In this contribution, our motivation for a systematic study on the optoelectronic properties of $\pi$-conjugated polymers containing the $\alpha,\beta$-unsubstituted meso-positioning thienyl BODIPY, as electron deficient unit, has led on the synthesis of two ultra LBG quaterthiophene polymers consisting of the $\alpha,\beta$-unsubstituted meso-positioning thienyl BODIPY (Figure 2).

![Chemical structure of the targeted $\alpha,\beta$-unsubstituted meso-positioning thienyl BODIPY building block (in blue) and those of the synthesized quaterthiophene polymers in the inner (i) (BODIPY-qT$i$) and outer (o) (BODIPY-qT$o$) positions of the didodecyl side chains consisting of the $\alpha,\beta$-unsubstituted meso-positioning thienyl BODIPY.]

Furthermore, special attention has been devoted on the positioning [head-to head (HH) or tail-to tail (TT)] of the two dodecyl side chain in the two central thiophene rings of the quaterthiophene.

In the inner (i) positions (TT positioning) when the didodecyl side chains are placed closer to the
BODIPY (BODIPY-qi) and the outer (o) positions (HH positioning) when the didodecyl side chains are placed further from the BODIPY (BODIPY-qTo) (Figure 2). It will be shown how the HH or TT positioning of the didodecyl side chains are affecting the optoelectronic, electrochemical and charge transporting properties of the corresponding BODIPY-qi and BODIPY-qTo.

2. Results and Discussion

2.1. Molecular Design, Monomer and Polymer Synthesis

The development of BODIPY-based organic semiconductors and especially those of the α,β- unsubstituted forms has so far lagged behind that of other π-deficient units, mainly because of stability issues during the synthesis. However, thanks to a recently developed synthetic protocol,37 a stable α,β-unsubstituted BODIPYs functionalized solely on the meso position with a thienyl group has been successfully synthesized (Figure 2) and integrated into more complex structures. The structural and electronic properties of the recently developed building block along with its structural analogues containing dimethyl substituents at the α-positions and tetramethyl substituents at the α,β-positions were determined via quantum chemical density functional theory (DFT) calculations utilizing the B3LYP/6-311G(d,p) as the model basis set and the results are presented in Figure 3. As shown in Figure 3, on the one hand the π-electron density of the highest occupied molecular orbital energy level (EHOMO) of all the three studied BODIPY monomers is found to be delocalized only on the dipyrromethene core (without the participation of the N-B(F2)-N sequence) along with the methyl groups in the case of the α-substituted meso-positioning thienyl BODIPY and the α,β-substituted meso-positioning thienyl BODIPY. On the other hand, the π-electron density of the lowest unoccupied molecular orbital energy level (ELUMO) is not only distributed throughout the boron-dipyrromethene core but is also found to be extended towards the meso-thienyl unit as the methyl substitution decreases. In addition, it is evident that as the number
of the methyl substituents decreases both the $E_{HOMO}$ and $E_{LUMO}$ levels are downshifted \textit{vs} vacuum due to the elimination of the $\sigma$-inductive effect of the methyl groups, but no significant variation is detected on the calculated $E_{HOMO} - E_{LUMO}$ gap. Furthermore, the subsequent exclusion of the methyl substituents from the $\alpha$- and $\beta$-positions leads to the reduction of the dihedral angle between the boron dipyrromethene core and the \textit{meso}-thienyl unit from 89.8° for the $\alpha,\beta$-substituted \textit{meso}-positioning thienyl BODIPY to 50.7° for the $\alpha$-substituted \textit{meso}-positioning thienyl BODIPY and finally to 47.3° for the $\alpha,\beta$-unsubstituted \textit{meso}-positioning thienyl BODIPY. The reduction of the dihedral angle, especially in the $\alpha,\beta$-unsubstituted \textit{meso}-positioning thienyl BODIPY, could contribute to the efficient $\pi-\pi$ stacking and C-H-\ldots-$\pi$ interactions when this building block would be integrated into $\pi$-conjugated polymer backbones.

**Fig. 3** Calculated frontier molecular orbital ($E_{HOMO}$/$E_{LUMO}$) levels, molecular dipole moments ($\mu$), dihedral angles between the boron dipyrromethene core with the \textit{meso}-thienyl ring and pictorial representations of the model monomers $\alpha,\beta$-unsubstituted \textit{meso}-positioning thienyl BODIPY, $\alpha$-substituted \textit{meso}-positioning thienyl BODIPY and the $\alpha,\beta$-substituted \textit{meso}-positioning thienyl BODIPY (B3LYP/6-311G(d,p) level of theory).
Among the other electron deficient units (1-10) presented in Figure 1, α,β-unsubstituted meso-positioning thienyl BODIPY apart from the facile synthesis (2 reaction steps) exhibits some other advantageous structural/electronic properties such as co-planarity, low $E_{\text{LUMO}}$ level and high dipole moment ($\mu$) as shown in Figures S1-S10 in electronic supplementary information (ESI). For instance, the $\mu$ of the α,β-unsubstituted meso-positioning thienyl BODIPY (6.54 D) is higher than those of the α-substituted BODIPY (4.86 D) and the α,β-substituted BODIPY (5.07 D) and one of the highest estimated between 1-10 (only 8 and 9 present higher values). The $\mu$ of the α,β-unsubstituted meso-positioning thienyl BODIPY (6.54 D) is higher than that of the α,β-substituted BODIPY (5.07 D) due to the absence of the methyl groups that decrease the electron affinity of the BODIPY core through their $\sigma$-inductive effect. In addition, the symmetric α,β-unsubstituted and α,β-substituted meso-positioning thienyl BODIPY monomers present higher $\mu$ than the asymmetric α-substituted BODIPY (4.86 D). Therefore, the higher $\mu$ value of the α,β-unsubstituted meso-positioning thienyl BODIPY is expected to enhance the backbone-ordering and as a consequence the crystallinity of the corresponding $\pi$-conjugated polymers thin films as a result of strong dipolar interactions.32

The synthetic procedure for the preparation of BODIPY-qTi and BODIPY-qTo is depicted in Scheme 1. The synthesis of 2,6-dibromo α,β-unsubstituted meso-positioning (5-octylthien-2-yl) BODIPY 13 is described in a recently developed synthetic protocol by our group.37 Briefly, condensation of the 5-octylthiophene-2-carbaldehyde with pyrrole, catalyzed by few drops of trifluoroacetic acid, provides the 2,2′-((5-octylthien-2-yl)methylene)bis(1H-pyrrole) 11. Treatment of 11 with the strong oxidant 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), then diisopropylethylamine (Hünig’s base) and finally with boron trifluoride etherate [BF$_3$O(Et)$_2$] affords the corresponding α,β-unsubstituted meso-positioning (5-octylthien-2-yl) BODIPY 12. Bromination of 12 with N-bromosuccinimide (NBS) using dimethylformamide (DMF):methylene
chloride (CH₂Cl₂) 1:1 as the solvent mixture results in compound 13. Then, Stille cross-coupling reaction between 13 and 2-tributylstannylthiophene utilizing tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃] in 2% per mole and tri(o-tolyl)phosphine (P(o-tol)₃), 4% per mole, as the catalytic system in toluene (PhMe) at ca. 120°C leads to the D-A-D type monomer dithienyl α,β-unsubstituted meso-positioning (5-octylthien-2-yl) BODIPY 14, which was then brominated by NBS in DMF at room temperature to provide the targeted dibromo dithienyl α,β-unsubstituted meso-positioning (5-octylthien-2-yl) BODIPY 15.

Scheme 1. Synthetic procedure for the preparation of the new designed monomer and the corresponding BODIPY-qTi and BODIPY-qTo polymers.
Stille coupling mediated polymerisation\textsuperscript{53} ([Pd\textsubscript{2}(dba)\textsubscript{3}] (2 mol %), [P(o-tol)\textsubscript{3}] (4 mol %) in PhMe at ca. 120 °C for 48 h) was used to combine the BODIPY precursor \textsuperscript{15} with readily available (4,4'-didodecyl-2,2'-bithiophene-5,5'-diyl)bis(trimethylstannane) \textsuperscript{16} or (3,3'-didodecyl-2,2'-bithiophene-5,5'-diyl)bis(trimethylstannane) \textsuperscript{17} to provide the polymers BODIPY-$q$Ti or BODIPY-$q$To, respectively (Scheme 1). The crude polymers as received from the reaction mixtures were purified by successive Soxhlet extractions and they were collected by precipitation from the chloroform (CF) fraction (BODIPY-$q$To) and chlorobenzene (CB) fraction (BODIPY-$q$Ti). The average molecular weights per number ($\overline{M}_n$), per weight ($\overline{M}_w$) and dispersity ($D$) of the polymers as measured by gel permeation chromatography (GPC) relative to monodispersed polystyrene standards at high temperature (150 °C) with 1,2-dichlorobenzene (DCB) as eluent are presented in Figures S19, S20 (ESI). While both polymers exhibit monomodal GPC profiles with no appearance of residual monomers or oligomer chains a noticeable effect of the didodecyl side chains positioning on the molecular characteristics has been observed. BODIPY-$q$To exhibits $\overline{M}_n$ of 72000 g/mol, with $D$ of 1.57, which is significantly higher than that of BODIPY-$q$Ti ($\overline{M}_n$ = 22380 g/mol, with $D$ = 1.74). Since that BODIPY-$q$Ti is received from the CB fraction it seems that anchoring the didodecyl side chains on the \textit{o}-positions prevent the easy solubility of the polymer chains in common organic solvents, which could explain the lower $\overline{M}_n$ of BODIPY-$q$Ti.

2.2. Optical and Electrochemical Properties

The absorption spectra of the BODIPY-$q$Ti and BODIPY-$q$To in ortho-dichlorobenzene (\textit{o}-DCB) solution are presented in Figure 4a and their corresponding optoelectronic characteristics are summarized in Table 1. BODIPY-$q$Ti and BODIPY-$q$To display qualitatively similar spectral shape with two well resolved vibronic transitions (Figure 4a). The low-wavelength peak observed at 426 nm for BODIPY-$q$Ti and at 424 nm for BODIPY-$q$To can be attributed to the polymers
backbone $\pi$-$\pi^*$ transition while the high-wavelength transition at 739 nm for BODIPY-qTi and at 715 nm for BODIPY-qTo is related to an intramolecular D-A charge transfer excitation.\textsuperscript{54}

![Absorption spectra](image)

**Fig. 4** a) Absorption spectra in solution and as thin films of BODIPY-qTi and BODIPY-qTo polymers. b) Room temperature μPL spectra following excitation at 543 nm of the BODIPY-qTo (black line) and BODIPY-qTi (red line) polymers. c, d) Normalized optical density vs wavelength plots at various time delays of BODIPY-qTo (c) and BODIPY-qTi (d), following photo-excitation at 1026 nm with a pump fluence of 1.5 mJ cm\textsuperscript{-2}.

<table>
<thead>
<tr>
<th>polymer</th>
<th>$\lambda_{\max}^\text{sol}$ [nm]</th>
<th>$\lambda_{\max}^\text{film}$ [nm]</th>
<th>$E_g^\text{opt}$ [eV]</th>
<th>$E^\text{ox}$ [V]</th>
<th>$E^\text{HOMO}$ [eV]</th>
<th>$E^\text{red}$ [V]</th>
<th>$E^\text{LUMO}$ [eV]</th>
<th>$E_g^\text{CV}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BODIPY-qTi</td>
<td>426, 739</td>
<td>446, 782, 877</td>
<td>0.85</td>
<td>0.62</td>
<td>-5.32</td>
<td>-0.63</td>
<td>-4.07</td>
<td>1.25</td>
</tr>
<tr>
<td>BODIPY-qTo</td>
<td>424, 715</td>
<td>415, 739</td>
<td>0.98</td>
<td>0.69</td>
<td>-5.39</td>
<td>-0.61</td>
<td>-4.09</td>
<td>1.30</td>
</tr>
</tbody>
</table>
Passing from solution to the solid state (Figure 4a), both the low- and high-wavelength absorption peaks of BODIPY-qTi and BODIPY-qTo are red shifted with respect to their solution spectra, except for the low wavelength absorption peak of BODIPY-qTo (Table 2). This supports the efficient \(\pi-\pi\) stacking of the polymer chains of BODIPY-qTi passing from solution to the solid state. In general, the same trends observed in solution for the BODIPY-qTi and BODIPY-qTo regarding the variation of the absorption maxima of both the low and high wavelength peaks were also observed in the solid state studies (446/782 nm for BODIPY-qTi and 415/739 nm for BODIPY-qTo). However, BODIPY-qTi reveals a pronounced absorption peak at longer wavelength (877 nm), a signature of a vibronic feature which denotes enhanced aggregate formation similar to that observed in regioregular poly(3-hexylthiophene) thin films, indicating a more ordered structure.\(^{55}\) Furthermore, the optical bandgap (\(E_{\text{g, opt}}\)) of BODIPY-qTi and BODIPY-qTo (Table 1) support that these polymers are ultra LBG polymeric semiconductors. The \(E_{\text{g, opt}}\) of BODIPY-qTi (0.85 eV) is lower by 0.13 eV than that of BODIPY-qTo (0.98 eV). Therefore, when the didodecyl side chains are anchored onto the HH positions in BODIPY-qTo the absorption peak maxima both in solution and in solid state are appeared at lower wavelengths and the \(E_{\text{g, opt}}\) is higher as compared to BODIPY-qTi, indicating a higher degree of steric hindrance and polymer chain distortion.

To support our assumption quantum chemical DFT calculations were performed to estimate the dihedral angles, to predict the molecular energy levels and model the distribution of the frontier molecular orbitals of the BODIPY-qTi and BODIPY-qTo. The DFT calculations using the B3LYP/6-311G(d,p) performed on trimer model compounds and the chemical structures of the BODIPY-qTi and BODIPY-qTo as obtained by the theoretical calculations are presented in Figure S11 (ESI) and the estimated dihedral angles in Table 2. The obtained results show that BODIPY-qTi and BODIPY-qTo present comparable estimated dihedral angles except in the case
of $\theta_2$ dihedral angle where the rotation between the adjacent units in BODIPY-qTo is 63.4° as compared to 20.9° in BODIPY-qTi. The lower $\theta_2$ dihedral angle between the adjacent didodecyl thiophene rings of BODIPY-qTi results in reduced steric hindrance along the axis when the didodecyl alkyl chains are TT positioning, which is beneficial towards enhanced optoelectronic and charge transporting properties. These findings are in agreement with the aforementioned observation on the absorption maxima and $E_g^{opt}$ variation (Figure 4 and Table 1) for BODIPY-qTi and BODIPY-qTo.

Table 2 Calculated dihedral angles ($\theta_1$, $\theta_2$, $\theta_3$, $\theta_4$ and $\theta_5$) of some representative bonds that are shown in Figure S11 (ESI) for the studied BODIPY-qTi and BODIPY-qTo polymers.

<table>
<thead>
<tr>
<th></th>
<th>$\theta_1$</th>
<th>$\theta_2$</th>
<th>$\theta_3$</th>
<th>$\theta_4$</th>
<th>$\theta_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BODIPY-qTi</td>
<td>33.2°</td>
<td>20.9°</td>
<td>30.5°</td>
<td>18.1°</td>
<td>16.8°</td>
</tr>
<tr>
<td>BODIPY-qTo</td>
<td>23.8°</td>
<td>63.4°</td>
<td>21.4°</td>
<td>19.2°</td>
<td>20.1°</td>
</tr>
</tbody>
</table>

In Figure 4b, the micro-photoluminescence (µPL) spectra of both polymers is presented, where one can observe significant quenching (∼20%) for the BODIPY-qTi polymer relative to the BODIPY-qTo one, while no significant µPL peak shift is noticed. This finding is rationalized if one considers the better $\pi$-$\pi$ stacking of the BODIPY-qTi polymer chains due to the reduced steric hindrance as compared to the BODIPY-qTo. Notably, the sharp peak at ca. 590 nm (2.1 eV) corresponds to the Raman signature of the symmetric vibration, $v_s$($\text{C=C}$), of the carbon-carbon double bond within the thiophene ring at 1450 cm$^{-1}$.57

The pristine polymers BODIPY-qTo and BODIPY-qTi were also studied by means of transient absorption spectroscopy (TAS) in order to examine the photo-excitation dynamic processes that occur following 1026 nm laser excitation. It is worth to mention that at least two-photon absorption
is used in order to excite these polymers, because the energy of the employed fundamental wavelength, i.e. 1026 nm, is lower than the energy an electron needs to move from the HOMO to LUMO of the polymers in question. Figures 4c and 4d present the normalized delta optical density (ΔOD) vs. wavelength, for the two polymers studied (BODIPY-qTo and BODIPY-qTi) as a function of time, i.e. following photo-excitation at t=0 fs. It becomes apparent from Figures 4c and 4d that for both polymers the dominant transient photo-induced absorption (ΔOD) peak shifts to higher wavelengths, i.e. lower energies, as time progresses. Namely, within 200 fs, the BODIPY-qTo polymer peak shifts from 550 to 663 nm, while the corresponding peak of BODIPY-qTi polymer shifts from 550 to 646 nm, respectively. This ultrafast red shift in both polymers is attributed to temporal post photo-excitation phenomena such as thermalization of the electrons and holes to the edge of the conduction and valence band, as well as, to the internal vibrational and rotational relaxations within the excited states.58-61

To estimate the energy levels and the electrochemical bandgap (EgCV) by identifying the oxidation and reduction potentials of the BODIPY-qTi and BODIPY-qTo, cyclic voltammetry (CV) has been performed (Figure 5 and Table 1). For comparison purposes, the reduction potentials of the well-known organic semiconductor fullerene derivative [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) with strong electron withdrawing characteristics have been also determined by CV (Figure 5 and Table 1). As shown in Figure 5, both BODIPY-qTi and BODIPY-qTo exhibit reversible oxidation and reduction peaks. The oxidation (Eox) and reduction (Ered) potentials are calculated by [(Epc+Ep,a)/2] where Epc and Ep,a are the cathodic and anodic peak potentials, respectively. It is demonstrated that the oxidation and reduction potentials of the polymers are alkyl side chain positioning dependent. BODIPY-qTi and BODIPY-qTo present oxidation/reduction potentials at 0.62 V/-0.63 V vs saturated calomel electrode (SCE) the former and at 0.69 V/-0.61 V vs SCE the latter. These lead to EHOMO/ELUMO levels at -5.32 eV/-4.07 eV for the BODIPY-qTi
and at -5.39 eV/-4.09 eV for the BODIPY-qTi vs vacuum resulting to very low $E_g^{CV}$ of 1.25 eV for the BODIPY-qTi and of 1.30 eV for the BODIPY-qTo. The obtained $E_g^{CV}$ of the polymers are increased by 0.4 eV (BODIPY-qTi) and 0.32 eV (BODIPY-qTo) than their corresponding $E_g^{opt}$ in agreement with recently reported results on other polymer systems.\textsuperscript{62} It is obvious that when the didodecyl side chains are anchored onto the TT positioning both the $E_{HOMO}/E_{LUMO}$ levels are upshifted as compared to BODIPY-qTo. A tentative explanation for the lower $E_{HOMO}/E_{LUMO}$ levels of BODIPY-qTo can be attributed to the steric constraints that prevent planarity of the quaterthiophene segment when the didodecyl alkyl chains of the two central thiophene units are anchored in the HH positioning in agreement with the findings on the optical properties (Figure 4 and Table 1) and the computational calculations (Figure S11 (ESI) and Table 2). Furthermore, PC71BM presents three reversible reduction peaks at -0.68 V, -1.06 V and -1.56 V vs SCE that are attributed to $E_{LUMO}$ (-4.02 eV), $E_{LUMO+1}$ (-3.64 eV) and $E_{LUMO+2}$ (-3.14 eV), respectively. These results show that the $E_{LUMO}$ levels of the BODIPY-qTi and BODIPY-qTo are lying lower by 0.05 eV (BODIPY-qTi) and 0.07 eV (BODIPY-qTo) as compared to PC71BM. The combined low $E_{LUMO}$ levels and small bandgaps ($E_g^{CV}$ and $E_g^{opt}$) are indicative of the highly electron-deficient and $\pi$-conjugated nature of the $\alpha,\beta$-unsubstituted meso-positioning thienyl BODIPY. These are among the lowest $E_{LUMO}$ levels reported to date for a semiconducting polymer comparable to those of the 2,2′-(bisindenofluorene-12,15-diylidene) dimalononitrile-based quaterthiophenes\textsuperscript{16c,d} and approaching those of air-stable $n$-channel core-cyanated perylene-, anthracene- and naphthalene-based small molecule semiconductors.\textsuperscript{63} Finally, the predicted $E_{HOMO}$ and $E_{LUMO}$ levels as well as the distribution of the frontier molecular orbitals of the BODIPY-qTi and BODIPY-qTo are presented in Figure 5. It is possible to observe that in BODIPY-qTi and BODIPY-qTo the $E_{HOMO}$ levels are fully delocalized along the polymer chain axis in contrast to the significant localization of the $E_{LUMO}$ on the $\alpha,\beta$-unsubstituted meso-positioning thienyl BODIPY along with a good
agreement in the variation between the theoretically predicted and the experimentally determined $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ levels.

![Fig. 5 Schematic illustration of the calculated frontier molecular orbital $E_{\text{HOMO}}$ (orange band) and $E_{\text{LUMO}}$ (blue band) levels variation and pictorial representations of the trimer model compounds BODIPY-qTi and BODIPY-qTo (B3LYP/6-311G(d,p) level of theory). With black lines the experimentally determined $E_{\text{HOMO}}/E_{\text{LUMO}}$ levels of BODIPY-qTi, BODIPY-qTo and PC$_{71}$BM via the cyclic voltammetry graphs during oxidation (left) and reduction (right).](image)

2.3. Charge Transporting Properties

The charge transport properties of all polymers were investigated in thin-film transistor devices. Measurements were performed using a bottom-contact (BC), top-gate device configuration with
gold (Au) source-drain electrodes. Polymer films were cast by spin-coating and subsequently annealed at 100 °C before the deposition of fluorinated ether (Cytop) gate dielectric inside a nitrogen filled glovebox. Both polymers exhibited $p$-type behaviour but significant differences were observed in their performance. In particular, the transfer and output characteristics of BODIPY-$q$Ti based transistors (Figures 6a,b) exhibited little hysteresis between the forward and reverse gate voltage ($V_G$) and source-drain voltage ($V_D$) sweeps, with a threshold voltage ($V_{TH}$) of around -15 V. The saturated charge carrier mobility value extracted from the transfer curves was relatively modest and around $5\times10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ (Figure 6c).

Fig. 6 Transfer (a), output (b) characteristics of BC/TG configuration OFET device and mobility calculation based on first derivative of the linear regime transfer curve and first derivative of the square root of the saturation regime transfer curve (c) for the BODIPY-$q$Ti.
In contrast, transistors based on BODIPY-qTo exhibited significantly larger hysteresis, with a much higher $V_{\text{TH}}$ of around -50 V (Figures S21a,b (ESI)). The poor device characteristics made it difficult to extract robust mobility values, although they were approximately one order of magnitude lower than the value extracted for BODIPY-qTi (Figure S21c (ESI)). One possible explanation for the reduced performance is the combination of the HH alkyl chains causing a large torsional twist in the conjugated backbone, inhibiting the close packing of the polymer chains, as well as the resulting increase in ionisation potential, which increases the injection barrier for holes.

**Table 3** Summary of the FET performance of BODIPY-qTi and BODIPY-qTo polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\mu_{\text{sat average}}$ ($\mu_{\text{sat max}}$) (cm V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_{\text{lin average}}$ (cm V$^{-1}$ s$^{-1}$)</th>
<th>$V_{\text{TH}}$ (V)</th>
<th>$I_{\text{on}} / I_{\text{off}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BODIPY-qTi</td>
<td>$4.7 \times 10^{-4} \pm 3.1 \times 10^{-5}$ (4.9 $\times 10^{-4}$)</td>
<td>$3.5 \times 10^{-4} \pm 3.8 \times 10^{-5}$</td>
<td>-14.4 ± 0.6</td>
<td>$10^2$ - $10^3$</td>
</tr>
<tr>
<td>BODIPY-qTo</td>
<td>$10^{-5} - 10^{-4}$</td>
<td>$10^{-5} - 10^{-4}$</td>
<td>&lt; -50 V</td>
<td>$10^{-2}$</td>
</tr>
</tbody>
</table>

Despite the low-lying LUMO of both polymers, no obvious evidence for electron transport was observed in these devices. In order to improve the electron injection, the Au source/drain electrodes were replaced with aluminium (Al) in an otherwise identical device configuration, since the latter has a lower work function that could potentially facilitate electron injection from the metal to the semiconductor due to the reduced barrier. Despite the improvement and the matching electrode/LUMO interface energetics, no electron accumulation could be observed. Since the nature of the dielectric/semiconductor interface is also known to have a dramatic influence on the electron transport across the channel, top-contact, bottom-gate devices were fabricated using the divinyltetramethyldisiloxane-bis-benzocyclobutene (BCB) as the gate dielectric since the latter is
known to provide a trap-free interface with various high electron mobility organic semiconductors. Control devices using the fullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) as the semiconductor were also prepared in the same device configuration. The latter samples demonstrated the expected transistor performance and in accordance with previously published data. However, we were unable to observe electron transport in either of the polymer devices (Figure S22 (ESI)). We therefore conclude that despite the low lying LUMO, neither of the polymers is a good electron transporting material. We believe this may be related to the poor delocalisation of the LUMO along the polymer backbone. However, the presence of unknown chemical impurities that act as electron traps and/or the influence of the layer microstructure may both play a role as well. However, detailed analysis of these effects is beyond the scope of this work and should be the subject of future investigations.

3. Conclusion

New ultra low bandgap (E₉,opt < 1 eV) π-conjugated D-A polymers consisting of α,β-unsubstituted meso-positioning thienyl BODIPY as electron deficient unit and quarterthiophene segment as electron donating unit have been successfully synthesized by palladium catalyzed Stille aromatic cross coupling polymerization condition. Moreover, it is demonstrated that the TT positioning of the alkyl side chains at the two central thiophenes of the quaterthiophene segment results to superior FET performance than the HH positioning due to the less steric hindrance of the polymer backbone. In addition, the lower torsional twist in the conjugated backbone of BODIPY-qTi leads to lower E₉,opt and upshifted energy levels versus vacuum as compared to BODIPY-qTo. Finally, even though the synthesized polymers exhibit strong electron affinity, higher than that of the PC₇₁BM, they present only p-type behaviour in FETs independent to the alkyl side chain.
positioning. We envision these insights will guide the synthetic chemists and materials scientists towards the optimization of next generation BODIPY-based polymeric semiconductors with predetermined optoelectronic properties for specific optoelectronic applications.

4. Experimental

Instrumentation, theoretical calculations, synthesis of monomers and polymers, $^1$H-, $^{13}$C- nuclear magnetic resonance (NMR) and mass spectroscopy of monomers, gel permeation chromatography (GPC) of polymers, absorption spectra of the monomers as well as the transport characteristics of the devices are given in the ESI.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


Development of new ultra low bandgap \( (E_{g}^{\text{opt}} < 1 \text{ eV}) \) \( \pi \)-conjugated D-A polymers consisting of \( \alpha,\beta \)-unsubstituted meso-positioning thienyl BODIPY