Journal of Materials Chemistry C

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: B. Squeo, V. G. Gregoriou, Y. Han, A. Palma-Cando, S. Allard, E. Serpetzoglou, I. Konidakis, E. Stratakis, A. Avgeropoulos, T. D. Anthopoulos, M. Heeney, U. Scherf and C. L. Chochos, *J. Mater. Chem. C*, 2018, DOI: 10.1039/C7TC05900K.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

α,β -Unsubstituted *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

Benedetta M. Squeo,^[a] Vasilis G. Gregoriou,^[a,b] Yang Han^[c] Alex Palma-Cando,^[d] Sybille Allard,^[d] Efthymis Serpetzoglou,^[e] Ioannis Konidakis,^[e] Emmanuel Stratakis,^[e] Apostolos Avgeropoulos,^[f] Thomas D. Anthopoulos,^[g,h] Martin Heeney,^[c] Ullrich Scherf,^[d] Christos L. Chochos^{[a,f]*}

^[a] Advent Technologies SA, Patras Science Park, Stadiou Street, Platani-Rio, 26504, Patra, Greece.

^[b] National Hellenic Research Foundation (NHRF), 48 Vassileos Constantinou Avenue, Athens 11635, Greece.

^[c] Department of Chemistry and Centre for Plastic Electronics, Imperial College London, Exhibition Road, South Kensington, London, SW7 2AY, UK.

^[d] Macromolecular Chemistry Group (buwmakro) and Institute for Polymer Technology, Bergische Universität Wuppertal, Gaußstraße 20, D-42119 Wuppertal, Germany.

^[e] Institute of Electronic Structure and Laser, Foundation for Research and Technology – Hellas, P. O. Box 1527, Heraklion, Crete, Greece

^[f] Department of Materials Science Engineering, University of Ioannina, Ioannina 45110, Greece.

^[g] Department of Physics and Centre for Plastic Electronics, Imperial College London, Exhibition Road, South Kensington, London, SW7 2AY, UK.

^[h] Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia.

*E-mail address: cchochos@advent-energy.com

Abstract

It is demonstrated that α,β -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) π -conjugated D-A quaterthiophene polymers. Furthermore, it is revealed that the optoelectronic, electrochemical and charge transporting properties of the resulting α,β -unsubstituted *meso*-positioning thienyl BODIPY quaterthiophene-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 quaterthiophene segment results to lower E_g^{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-C₇₁-butyric acid methyl ester (PC₇₁BM), 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, ¹H-, ¹³C- 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.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.⁷⁻²³ One of the most promising class of LBG π -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),^{7d} benzobisthiadiazole (2),^{7h} diketopyrrolopyrrole (3),^{8e-g} phenanthrene (4)^{15a} or benzodithiophene (5)^{15c} condensed thiadiazoloquinoxaline, indeno[1,2-*b*]fluorene-6,12-dione (6),^{16c} 2,2'-(indeno[1,2-*b*]fluorene-6,12-diylidene) dimalononitrile (7),^{16c} bisindenofluorene-12,15-dione (8),^{16c} 2,2'-(bisindenofluorene-12,15-diylidene) dimalononitrile (9)^{16c,d} and fused aromatic thieno[3,4-*b*]pyrazine (10)^{22c} (Figure 1).

Fig. 1 General chemical structures of donor-acceptor (D-A) π -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 π -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 π -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, α,β -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- 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 α,β -unsubstituted BODIPY functionalized with thienyl group at the *meso*-position is possible, resulting to an ultra LBG (1.15 eV) π -conjugated polymer that was employed as electron donor material in NIR OPVs.³⁷ In this contribution, our motivation for a systematic study on the optoelectronic properties of π -conjugated polymers containing the α,β -unsubstituted *meso*-positioning thienyl BODIPY, as electron deficient unit, has led on the synthesis of two ultra LBG quaterthiophene polymers consisting of the α,β -unsubstituted *meso*-positioning thienyl BODIPY (Figure 2).

Fig. 2 Chemical structure of the targeted α,β -unsubstituted *meso*-positioning thienyl BODIPY building block (in blue) and those of the synthesized quaterthiophene polymers in the inner (i) (BODIPY-qTi) and outer (o) (BODIPY-qTo) positions of the didodecyl side chains consisting of the α,β -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-qTi**) 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-qTi 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 (E_{HOMO}) 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 (E_{LUMO}) 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 vs vacuum due to the elimination of the σ -inductive effect of the methyl groups, but no significant variation is detected on the calculated $E_{\text{HOMO}}-E_{\text{LUMO}}$ gap. Furthermore, the subsequent exclusion of the methyl substituents from the α - and β -positions leads to the reduction of the dihedral angle between the boron dipyrromethene core and the *meso*-thienyl unit from 89.8° for the α,β -substituted *meso*-positioning thienyl BODIPY to 50.7° for the α -substituted *meso*-positioning thienyl BODIPY and finally to 47.3° for the α,β -unsubstituted *meso*-positioning thienyl BODIPY. The reduction of the dihedral angle, especially in the α,β -unsubstituted *meso*-positioning thienyl BODIPY, could contribute to the efficient π - π stacking and C-H $\cdots\pi$ interactions when this building block would be integrated into π -conjugated polymer backbones.

Fig. 3 Calculated frontier molecular orbital ($E_{\text{HOMO}}/E_{\text{LUMO}}$) levels, molecular dipole moments (μ), dihedral angles between the boron dipyrromethene core with the *meso*-thienyl ring and pictorial representations of the model monomers α,β -unsubstituted *meso*-positioning thienyl BODIPY, α -substituted *meso*-positioning thienyl BODIPY and the α,β -substituted *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_{LUMO} level and high dipole moment (μ) as shown in Figures S1-S10 in electronic supplementary information (ESI). For instance, the μ 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 μ 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 σ -inductive effect. In addition, the symmetric α,β -unsubstituted and α,β -substituted *meso*-positioning thienyl BODIPY monomers present higher μ than the asymmetric α -substituted BODIPY (4.86 D). Therefore, the higher μ 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 π -conjugated polymers thin films as a result of strong dipolar interactions.⁵²

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(1*H*-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 [$\text{BF}_3\text{O}(\text{Et})_2$] 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 (CH_2Cl_2) 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) [$\text{Pd}_2(\text{dba})_3$] in 2% per mole and tri(*o*-tolyl)phosphine ($\text{P}(\text{o-tol})_3$), 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 polymerisation⁵³ ($[\text{Pd}_2(\text{dba})_3]$ (2 mol %), $[\text{P}(o\text{-tol})_3]$ (4 mol %) in PhMe at *ca.* 120 °C for 48 h) was used to combine the BODIPY precursor **15** with readily available (4,4'-didodecyl-2,2'-bithiophene-5,5'-diyl)bis(trimethylstannane) **16** or (3,3'-didodecyl-2,2'-bithiophene-5,5'-diyl)bis(trimethylstannane) **17** to provide the polymers **BODIPY-qTi** or **BODIPY-qTo**, 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-qTo**) and chlorobenzene (CB) fraction (**BODIPY-qTi**). The average molecular weights per number ($\overline{M}_n$), per weight ($\overline{M}_w$) and dispersity ($\overline{D}$) 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-qTo** exhibits $\overline{M}_n$ of 72000 g/mol, with $\overline{D}$ of 1.57, which is significantly higher than that of **BODIPY-qTi** ($\overline{M}_n$ = 22380 g/mol, with $\overline{D}$ = 1.74). Since that **BODIPY-qTi** is received from the CB fraction it seems that anchoring the didodecyl side chains on the *o*-positions prevent the easy solubility of the polymer chains in common organic solvents, which could explain the lower $\overline{M}_n$ of **BODIPY-qTi**.

2.2. Optical and Electrochemical Properties

The absorption spectra of the **BODIPY-qTi** and **BODIPY-qTo** in ortho-dichlorobenzene (*o*-DCB) solution are presented in Figure 4a and their corresponding optoelectronic characteristics are summarized in Table 1. **BODIPY-qTi** and **BODIPY-qTo** display qualitatively similar spectral shape with two well resolved vibronic transitions (Figure 4a). The low-wavelength peak observed at 426 nm for **BODIPY-qTi** and at 424 nm for **BODIPY-qTo** can be attributed to the polymers

backbone π - π^* 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.⁵⁴

Fig. 4 a) Absorption spectra in solution and as thin films of BODIPY-qTi and BODIPY-qTo polymers. b) Room temperature μ PL 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^{-2} .

Table 1 Optical and electrochemical properties of BODIPY-qTi and BODIPY-qTo.

polymer	$\lambda_{\text{max}}^{\text{sol}}$	$\lambda_{\text{max}}^{\text{film}}$	$E_{\text{g}}^{\text{opt}}$	E^{ox}	E_{HOMO}	E^{red}	E_{LUMO}	E_{g}^{CV}
	[nm]	[nm]	[eV]	[V]	[eV]	[V]	[eV]	[eV]
BODIPY-qTi	426, 739	446, 782, 877	0.85	0.62	-5.32	-0.63	-4.07	1.25
BODIPY-qTo	424, 715	415, 739	0.98	0.69	-5.39	-0.61	-4.09	1.30

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 π - π 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_g^{opt}) of **BODIPY-qTi** and **BODIPY-qTo** (Table 1) support that these polymers are ultra LBG polymeric semiconductors. The E_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_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 θ_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 θ_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.⁵⁶ 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 (θ_1 , θ_2 , θ_3 , θ_4 and θ_5) of some representative bonds that are shown in Figure S11 (ESI) for the studied **BODIPY-qTi** and **BODIPY-qTo** polymers.

	θ_1	θ_2	θ_3	θ_4	θ_5
BODIPY-qTi	33.2°	20.9°	30.5°	18.1°	16.8°
BODIPY-qTo	23.8°	63.4°	21.4°	19.2°	20.1°

In Figure 4b, the micro-photoluminescence (μPL) spectra of both polymers is presented, where one can observe significant quenching ($\sim 20\%$) 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 π - π 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, $\nu_s(\text{C}=\text{C})$, 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 (E_g^{CV}) 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 (E_{ox}) and reduction (E_{red}) potentials are calculated by $[(E_{p,c} + E_{p,a})/2]$ where $E_{p,c}$ and $E_{p,a}$ 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 E_{HOMO}/E_{LUMO} levels at -5.32 eV/-4.07 eV for the **BODIPY-qTi**

and at -5.39 eV/-4.09 eV for the **BODIPY-qTo** 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.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 π -conjugated nature of the α,β -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^{16c,d} and approaching those of air-stable *n*-channel core-cyanated perylene-, anthracene- and naphthalene-based small molecule semiconductors.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 α,β -unsubstituted *meso*-positioning thienyl BODIPY along with a good

agreement in the variation between the theoretically predicted and the experimentally determined E_{HOMO} and E_{LUMO} levels.

Fig. 5 Schematic illustration of the calculated frontier molecular orbital E_{HOMO} (orange band) and E_{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_{HOMO} / E_{LUMO} levels of BODIPY-qTi, BODIPY-qTo and PC₇₁BM via the cyclic voltammetry graphs during oxidation (left) and reduction (right).

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-qTi** 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 $5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (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-qTi.

In contrast, transistors based on **BODIPY-qTo** exhibited significantly larger hysteresis, with a much higher V_{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.

Polymer	μ_{sat} average (μ_{sat}^{max}) ($cm^2 V^{-1} s^{-1}$)	μ_{lin} average ($cm^2 V^{-1} s^{-1}$)	V_{Th} (V)	I_{on}/I_{off}
BODIPY-qTi	$4.7 \times 10^{-4} \pm 3.1 \times 10^{-5}$ (4.9×10^{-4})	$3.5 \times 10^{-4} \pm 3.8 \times 10^{-5}$	-14.4 ± 0.6	$10^2 - 10^3$
BODIPY-qTo	$10^{-5} - 10^{-4}$	$10^{-5} - 10^{-4}$	< -50 V	$10 - 10^2$

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.⁶⁴⁻⁶⁶ 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.⁶⁵ 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 ($E_g^{\text{opt}} < 1$ 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 E_g^{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, ^1H -, ^{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.

Acknowledgments

This project has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under the Grant Agreement n° 331389 project ECOCHEM, n° 607585 project OSNIRO and n° 604603 project MatHero. The authors would like to thank Anke Helfer from BUW for the mass spectrometry measurements.

Notes and references

1. L. Dou, Y. Liu, Z. Hong, G. Li and Y. Yang, *Chem Rev.*, 2015, **115**, 12633.
2. X. Guo, M. Baumgarten and K. Müllen, *Prog. Polym. Sci.*, 2013, **38**, 1832.
3. Z. Guo, S. Park, J. Yoon and I. Shin, *Chem. Soc. Rev.*, 2014, **43**, 16.
4. J. D. Yuen, R. Kumar, D. Zakhidov, J. Seifter, B. Lim, A. J. Heeger, F. Wudl, *Adv. Mater.*, 2011, **23**, 3780.
5. X. Guo, A. Facchetti and T. J. Marks, *Chem. Rev.*, 2014, **114**, 8943.
6. C. B. Nielsen, M. Turbiez and I. McCulloch, *Adv. Mater.*, 2013, **25**, 1859.
7. (a) J. D. Yuen, R. Kumar, D. Zakhidov, J. Seifter, B. Lim, A. J. Heeger and F. Wudl, *Adv. Mater.*, 2011, **23**, 3780; (b) J. Fan, J. D. Yuen, M. Wang, J. Seifter, J.-H. Seo, A. R. Mohebbi, D. Zakhidov, A. Heeger and F. Wudl, *Adv. Mater.*, 2012, **24**, 2186; (c) J. D. Yuen, J. Fan, J. Seifter, B. Lim, R. Hufschmid, A. J. Heeger and F. Wudl, *J. Am. Chem. Soc.*, 2011, **133**, 20799; (d) C. Yang, S. Cho, R. C. Chiechi, W. Walker, N. E. Coates, D. Moses, A. J. Heeger and F. Wudl, *J. Am. Chem. Soc.*, 2008, **130**, 16524; (e) W. Cui and F. Wudl, *Macromolecules*, 2013, **46**, 7232; (f) A. R. Mohebbi, J. Yuen, J. Fan, C. Munoz, M. F. Wang, R. S. Shirazi, J. Seifter and F. Wudl, *Adv. Mater.*, 2011, **23**, 4644; (g) J. D. Yuen and F. Wudl, *Energy Environ. Sci.*, 2013, **6**, 392; (h) J. Fan, J. D. Yuen, W. Cui, J. Seifter, A. R. Mohebbi, M. Wang, H. Zhou, A. J. Heeger and F. Wudl, *Adv. Mater.*, 2012, **24**, 6164.
8. (a) M. M. Wienk, M. G. R. Turbiez, M. P. Struijk, M. Fonrodona and R. A. J. Janssen, *Appl. Phys. Lett.*, 2006, **88**, 153511; (b) G. W. P. van Pruissen, F. Gholamrezaie, M. M. Wienk and R. A. J. Janssen, *J. Mater. Chem.*, 2012, **22**, 20387; (c) K. H. Hendriks, W. Li, M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2014, **136**, 12130; (d) A. P. Zoombelt, M. Fonrodona, M. M. Wienk, A. B. Sieval, J. C. Hummelen and R. A. J. Janssen, *Org. Lett.*, 2009, **11**, 903; (e) W. Li, K. H. Hendriks, A. Furlan, W. S. Christian Roelofs, M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2013, **135**, 18942; (f) M. M. Wienk, M. Turbiez,

- J. Gilot and R. A. J. Janssen, *Adv. Mater.*, 2008, **20**, 2556; (g) F. Liu, Y. Gu, C. Wang, W. Zhao, D. Chen, A. L. Briseno and T. P. Russell, *Adv. Mater.*, 2012, **24**, 3947.
9. (a) Y. Yao, Y. Liang, V. Shrotriya, S. Xiao, L. Yu and Y. Yang, *Adv. Mater.*, 2007, **19**, 3979; (b) L. Dou, C.-C. Chen, K. Yoshimura, K. Ohya, W.-H. Chang, J. Gao, Y. Liu, E. Richard and Y. Yang, *Macromolecules*, 2013, **46**, 3384; (c) L. Dou, W.-H. Chang, J. Gao, C.-C. Chen, J. You and Y. Yang, *Adv. Mater.*, 2013, **25**, 825.
10. Y. Xia, L. Wang, X. Deng, D. Li, X. Zhu and Y. Cao, *Appl. Phys. Lett.*, 2006, **89**, 081106
11. (a) P. M. Beaujuge, S. Ellinger and J. R. Reynolds, *Nat. Mater.*, 2008, **7**, 795; (b) T. T. Steckler, X. Zhang, J. Hwang, R. Honeyager, S. Ohira, X.-H. Zhang, A. Grant, S. Ellinger, S. A. Odom, D. Sweat, D. B. Tanner, A. G. Rinzler, S. Barlow, J.-L. Brédas, B. Kippelen, S. R. Marder and J. R. Reynolds, *J. Am. Chem. Soc.*, 2009, **131**, 2824.
12. (a) P.-T. Wu, F. S. Kim and S. A. Jenekhe, *Chem. Mater.*, 2011, **23**, 4618; (b) H. Li, F. S. Kim, G. Ren and S. A. Jenekhe, *J. Am. Chem. Soc.*, 2013, **135**, 14920; (c) H. Li, Y.-J. Hwang, T. Earmme, R. C. Huber, B. A. E. Courtright, C. O'Brien, S. H. Tolbert and S. A. Jenekhe, *Macromolecules*, 2015, **48**, 1759; (d) Y.-J. Hwang, F. S. Kim, H. Xin and S. A. Jenekhe, *Macromolecules*, 2012, **45**, 3732.
13. (a) T. T. Steckler, P. Henriksson, S. Mollinger, A. Lundin, A. Salleo and M. R. Andersson, *J. Am. Chem. Soc.*, 2014, **136**, 1190; (b) E. Wang, L. Hou, Z. Wang, S. Hellström, W. Mammo, F. Zhang, O. Inganäs and M. R. Andersson, *Org. Lett.*, 2010, **12**, 4470.
14. (a) T. L. D. Tam, T. Salim, H. Li, F. Zhou, S. G. Mhaisalkar, H. Su, Y. M. Lam and A. C. Grimsdale, *J. Mater. Chem.*, 2012, **22**, 18528; (b) T. L. D. Tam, W. Ye, H. H. R. Tan, F. Zhou, H. Su, S. G. Mhaisalkar and A. C. Grimsdale, *J. Org. Chem.*, 2012, **77**, 10035.

15. (a) M. Li, C. An, T. Marszalek, X. Guo, Y.-Z. Long, H. Yin, C. Gu, M. Baumgarten, W. Pisula and K. Müllen, *Chem. Mater.*, 2015, **27**, 2218; (b) T. Dallos, D. Beckmann, G. Brunklaus and M. Baumgarten, *J. Am. Chem. Soc.*, 2011, **133**, 13898; (c) C. An, S. R. Puniredd, X. Guo, T. Stelzig, Y. Zhao, W. Pisula and M. Baumgarten, *Macromolecules*, 2014, **47**, 979.
16. (a) H. Usta, C. Newman, Z. Chen and A. Facchetti, *Adv. Mater.*, 2012, **24**, 3678; (b) H. Huang, Z. Chen, R. P. Ortiz, C. Newman, H. Usta, S. Lou, J. Youn, Y.-Y. Noh, K.-J. Baeg, L. X. Chen, A. Facchetti and T. Marks, *J. Am. Chem. Soc.*, 2012, **134**, 10966; (c) H. Usta, C. Risko, Z. Wang, H. Huang, M. K. Delimeroglu, A. Zhukhovitskiy, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2009, **131**, 5586; (d) H. Usta, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2008, **130**, 8580.
17. (a) R. S. Ashraf, I. Meager, M. Nikolka, M. Kirkus, M. Planells, B. C. Schroeder, S. Holliday, M. Hurhangee, C. B. Nielsen, H. Sirringhaus and I. McCulloch, *J. Am. Chem. Soc.*, 2015, **137**, 1314; (b) R. S. Ashraf, A. J. Kronemeijer, D. I. James, H. Sirringhaus and I. McCulloch, *Chem. Commun.*, 2012, **48**, 3939; (c) H. Bronstein, E. Collado-Fregoso, A. Hadipour, Y. W. Soon, Z. Huang, S. D. Dimitrov, R. S. Ashraf, B. P. Rand, S. E. Watkins, P. S. Tuladhar, I. Meager, J. R. Durrant and I. McCulloch, *Adv. Funct. Mater.*, 2013, **23**, 5647; (d) I. Meager, M. Nikolka, B. C. Schroeder, C. B. Nielsen, M. Planells, H. Bronstein, J. W. Rumer, D. I. James, R. S. Ashraf, A. Sadhanala, P. Hayoz, J.-C. Flores, H. Sirringhaus and I. McCulloch, *Adv. Funct. Mater.*, 2014, **24**, 7109; (e) J. W. Rumer, M. Levick, S.-Y. Dai, S. Rossbauer, Z. Huang, L. Biniek, T. D. Anthopoulos, J. R. Durrant, D. J. Procter and I. McCulloch, *Chem. Commun.*, 2013, **49**, 4465; (f) H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J. R. Durrant, P. S. Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M.

- Wienk, R. A. J. Janssen, T. Anthopoulos, H. Sirringhaus, M. Heeney and I. McCulloch, *J. Am. Chem. Soc.*, 2011, **133**, 3272.
18. (a) Z. Fei, X. Gao, J. Smith, P. Pattanasattayavong, E. B. Domingo, N. Stingelin, S. E. Watkins, T. D. Anthopoulos, R. J. Kline and M. Heeney, *Chem. Mater.*, 2013, **25**, 59; (b) M. Shahid, T. McCarthy-Ward, J. Labram, S. Rossbauer, E. B. Domingo, S. E. Watkins, N. Stingelin, T. D. Anthopoulos and M. Heeney, *Chem. Sci.*, 2012, **3**, 181; (c) A. J. Kronemeijer, E. Gili, M. Shahid, J. Rivnay, A. Salleo, M. Heeney and H. Sirringhaus, *Adv. Mater.*, 2012, **24**, 1558.
19. (a) C. P. Yau, Z. Fei, R. S. Ashraf, M. Shahid, S. E. Watkins, P. Pattanasattayavong, T. D. Anthopoulos, V. G. Gregoriou, C. L. Chochos and M. Heeney, *Adv. Funct. Mater.*, 2014, **24**, 678; (b) C. L. Chochos, J. K. Kallitsis, P. E. Keivanidis, S. Balushev and V. G. Gregoriou, *J. Phys. Chem. B*, 2006, **110**, 4657.
20. (a) S. Cho, J. Lee, M. Tong, J. H. Seo and C. Yang, *Adv. Funct. Mater.*, 2011, **21**, 1910; (b) P. Sonar, S. P. Singh, Y. Li, M. S. Soh and A. Dodabalapur, *Adv. Mater.*, 2010, **22**, 5409.
21. (a) C. V. Hoven, X.-D. Dang, R. C. Coffin, J. Peet, T.-Q. Nguyen and G. C. Bazan, *Adv. Mater.*, 2010, **22**, E63; (b) G. C. Welch and G. C. Bazan, *J. Am. Chem. Soc.*, 2011, **133**, 4632; (c) L. Ying, B. B. Y. Hsu, H. Zhan, G. C. Welch, P. Zalar, L. A. Perez, E. J. Kramer, T.-Q. Nguyen, A. J. Heeger, W.-Y. Wong and G. C. Bazan, *J. Am. Chem. Soc.*, 2011, **133**, 18538.
22. (a) Z. Cai, H. Luo, P. Qi, J. Wang, G. Zhang, Z. Liu and D. Zhang, *Macromolecules*, 2014, **47**, 2899; (b) M. Karakawa and Y. Aso, *Macromol. Chem. Phys.*, 2013, **214**, 2388; (c) R. Mondal, N. Miyaki, H. A. Becerril, J. E. Norton, J. Parmer, A. C.

- Mayer, M. L. Tang, J.-L. Brédas, M. D. McGehee and Z. Bao, *Chem. Mater.*, 2009, **21**, 3618.
23. (a) R. Tautz, E. Da Como, T. Limmer, J. Feldmann, H.-J. Egelhaaf, E. von Hauff, V. Lemaure, D. Beljonne, S. Yilmaz, I. Dumsch, S. Allard and U. Scherf, *Nat. Commun.* 2012, **3**, 970; (b) H. Reisch, U. Wiesler, U. Scherf and N. Tuytuykov, *Macromolecules*, 1996, **29**, 8204; (c) C. J. Kudla, D. Dolfen, K. J. Schottler, J.-M. Koenen, D. Breusov, S. Allard and U. Scherf, *Macromolecules*, 2010, **43**, 7864.
24. (a) G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem. Int. Ed.*, 2008, **47**, 1184; (b) A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891; (c) M. Benstead, G. H. Mehl and R. W. Boyle, *Tetrahedron*, 2011, **67**, 3573.
25. B. M. Squeo, V. G. Gregoriou, A. Avgeropoulos, S. Baysec, S. Allard, U. Scherf and C. L. Chochos, *Prog. Polym. Sci.*, 2017, **71**, 26.
26. S. P. Economopoulos, C. L. Chochos, H. A. Ioannidou, M. Neophytou, C. Charilaou, G. A. Zissimou, J. M. Frost, T. Sachetan, M. Shahid, J. Nelson, M. Heeney, D. D. C. Bradley, G. Itskos, P. A. Koutentis and S. A. Choulis, *RSC Adv.*, 2013, **3**, 10221.
27. (a) B. Kim, B. W. Ma, V. R. Donuru, H. Y. Liu and J. M. J. Fréchet, *Chem. Commun.*, 2010, **46**, 4148; (b) R. Yoshii, H. Yamane, K. Tanaka and Y. Chujo, *Macromolecules*, 2014, **47**, 3755.
28. B. C. Popere, A. M. Della Pelle and S. Thayumanavan, *Macromolecules*, 2011, **44**, 4767.
29. (a) C. Thivierge, A. Loudet and K. Burgess, *Macromolecules*, 2011, **44**, 4012; (b) A. B. Nepomnyashchii, M. Bröring, J. Ahrens and A. J. Bard, *J. Am. Chem. Soc.*, 2011, **133**, 8633.

30. M. Zhu, L. Jiang, M. J. Yuan, X. F. Liu, C. B. Ouyang, H. Y. Zheng, X. D. Yin, Z. C. Zuo, H. B. Liu and Y. L. Li, *J. Polym. Sci. Polym. Chem.*, 2008, **46**, 7401.
31. S. L. Zhu, N. Dorh, J. T. Zhang, G. Vegesna, H. H. Li, F. T. Luo, A. Tiwari and H. Y. Liu, *J. Mater. Chem.*, 2012, **22**, 2781.
32. F. Algi and A. Cihaner, *Org. Electron.*, 2009, **10**, 453.
33. H. Usta, M. D. Yilmaz, A.-J. Avestro, D. Boudinet, M. Denti, W. Zhao, J. F. Stoddart and A. Facchetti, *Adv. Mater.*, 2013, **25**, 4327.
34. J. C. Forgie, P. J. Skabara, I. Stibor, F. Vilela and Z. Vobecka, *Chem. Mater.*, 2009, **21**, 1784.
35. M. D. Yilmaz, T. Aytun, M. Frasconi, S. I. Stupp and F. Stoddart, *Synth. Met.*, 2014, **197**, 52.
36. D. Cortizo-Lacalle, C. T. Howells, S. Gambino, F. Vilela, Z. Vobecka, N. J. Findlay, A. R. Inigo, S. A. J. Thomson, P. J. Skabara and I. D. W. Samuel, *J. Mater. Chem.*, 2012, **22**, 14119.
37. B. M. Squeo, N. Gasparini, T. Ameri, A. Palma-Caldo, S. Allard, V. G. Gregoriou, C. J. Brabec, U. Scherf and C. L. Chochos, *J. Mater. Chem. A*, 2015, **3**, 16279.
38. (a) T. Lei, J.-Y. Wang and J. Pei, *Chem. Mater.*, 2014, **26**, 594; (b) C. L. Chochos and S. A. Choulis, *Prog. Polym. Sci.*, 2011, **36**, 1326.
39. C. Wang, H. Dong, W. Hu, Y. Liu and D. Zhu, *Chem. Rev.*, 2012, **112**, 2208.
40. L. Ding, H.-B. Li, T. Lei, H.-Z. Ying, R.-B. Wang, Y. Zhou, Z.-M. Su and J. Pei, *Chem. Mater.*, 2012, **24**, 1944.
41. W. Li, K. H. Hendriks, A. Furlan, W. S. C. Roelofs, S. C. J. Meskers, M. M. Wienk and R. A. J. Janssen, *Adv. Mater.*, 2014, **26**, 1565.
42. T. Lei, J.-H. Dou and J. Pei, *Adv. Mater.*, 2012, **24**, 6457.

43. L. Biniek, S. Fall, C. L. Chochos, D. V. Anokhin, D. A. Ivanov, N. Leclerc, P. Lévêque and T. Heiser, *Macromolecules*, 2010, **43**, 9779.
44. C. L. Chochos, A. Katsouras, N. Gasparini, C. Koulogiannis, T. Ameri, C. J. Brabec and A. Avgeropoulos, *Macromol. Rapid Commun.*, 2017, **38**, 1600614.
45. X.-Y. Wang, F.-D. Zhuang, X. Zhou, D.-C. Yang, J.-Y. Wang and J. Pei, *J. Mater. Chem. C*, 2014, **2**, 8152.
46. H. Bronstein, D. S. Leem, R. Hamilton, P. Woebkenberg, S. King, W. Zhang, R. S. Ashraf, M. Heeney, T. D. Anthopoulos, J. deMello and I. McCulloch, *Macromolecules*, 2011, **44**, 6649.
47. Q. Wu, M. Wang, X. Qiao, Y. Xiong, Y. Huang, X. Gao and H. Li, *Macromolecules*, 2013, **46**, 3887.
48. R. J. Kline, D. M. DeLongchamp, D. A. Fischer, E. K. Lin, L. J. Richter, M. L. Chabinyc, M. F. Toney, M. Heeney and I. McCulloch, *Macromolecules*, 2007, **40**, 7960.
49. L. Biniek, S. Fall, C. L. Chochos, N. Leclerc, P. Lévêque and T. Heiser, *Org. Electron.*, 2012, **13**, 114.
50. F. Zhang, Y. Hu, T. Schuettfort, C. Di, X. Gao, C. R. McNeill, L. Thomsen, S. C. B. Mannsfeld, W. Yuan, H. Sirringhaus and D. Zhu, *J. Am. Chem. Soc.*, 2013, **135**, 2338.
51. I. Meager, R. S. Ashraf, S. Mollinger, B. C. Schroeder, H. Bronstein, D. Beatrup, M. S. Vezie, T. Kirchartz, A. Salleo, J. Nelson and I. McCulloch, *J. Am. Chem. Soc.*, 2013, **135**, 11537.
52. J. A. Letizia, M. R. Salata, C. M. Tribout, A. Facchetti, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2008, **130**, 9679.
53. B. Carsten, F. He, H. J. Son, T. Xu and L. Yu, *Chem. Rev.*, 2011, **111**, 1493.

54. S. Roquet, A. Cravino, P. Leriche, O. Alévêque, P. Frère and J. Roncali, *J. Am. Chem. Soc.*, 2006, **128**, 3459.
55. (a) T.-A. Chen, X. Wu and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233; (b) R. S. Loewe, P. C. Ewbank, J. Liu, L. Zhai and R. D. McCullough, *Macromolecules*, 2001, **34**, 4324
56. (a) X. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski and S. R. Marder, *Adv. Mater.*, 2011, **23**, 268; (b) J. Mei, Y. Diao, A. L. Appleton, L. Fang and Z. Bao, *J. Am. Chem. Soc.*, 2013, **135**, 6724.
57. P. M. Viruela, R. Viruela, E. Ortí, J. Casado, V. Hernández and J. T. L. Navarrete, *J. Mol. Struct.*, 2003, **651-653**, 657.
58. M. Maiuri, G. Grancini, D. Fazzi, H. J. Egelhaaf, D. Brida, G. Cerullo and G. Lanzani, *EPJ Web of Conferences*, 2013, **41**, 04010.
59. I. W. Hwang, Q. H. Xu, C. Soci, B. Q. Chen, A. K. Y. Jen, D. Moses and A. J. Heeger, *Adv. Funct. Mater.*, 2007, **17**, 563.
60. F. Deschler, E. Da Como, T. Limmer, R. Tautz, T. Godde, M. Bayer, E. von Hauff, S. Yilmaz, S. Allard, U. Scherf and J. Feldmann, *Phys Rev. Lett.*, 2011, **107**, 127402.
61. N. Banerji, S. Cowan, M. Leclerc, E. Vauthey and A. J. Heeger, *J. Am. Chem. Soc.* 2010, **132**, 17459.
62. K. Kawashima, Y. Tamai, H. Ohkita, I. Osaka and K. Takimiya, *Nat. Commun.*, 2015, **6**, 10085
63. (a) R. Schmidt, M. M. Ling, J. H. Oh, M. Winkler, M. Könemann, Z. Bao and F. Würthner, *Adv. Mater.*, 2007, **19**, 3692; (b) Z. Wang, C. Kim, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2007, **129**, 13362; (c) B. A. Jones, M. J. Ahrens, M. H. Yoon, A. Facchetti, T. J. Marks and M. R. Wasielewski, *Angew. Chem. Intl. Ed.*, 2004, **43**,

- 6363; (d) H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Seigrist, W. Li, Y.-Y. Lin and A. Dodabalapur, *Nature*, 2000, **404**, 478.
64. T. D. Anthopoulos, B. Singh, N. Marjanovic, N. S. Sariciftci, A. M. Ramil, H. Sitter, M. Cölle and D. M. de Leeuw, *Appl. Phys. Lett.*, 2006, **89**, 213504.
65. P. H. Wöbkenberg, D. D. C. Bradley, D. Kronholm, J. C. Hummelen, D. M. de Leeuw, M. Cölle and T. D. Anthopoulos, *Synth. Met.*, 2008, **158**, 468.
66. L.-L. Chua, J. Zaumseil, J.-F. Chang, E. C.-W. Ou, P. K.-H. Ho, H. Sirringhaus and R. H. Friend, *Nature*, 2005, **434**, 194.

Table of Content (TOC) Figure

Development of new ultra low bandgap ($E_g^{\text{opt}} < 1$ eV) π -conjugated D-A polymers consisting of α,β -unsubstituted *meso*-positioning thienyl BODIPY