PAPER

Synthesis and characterizations of red/near-IR absorbing A–D–A–D–A-type oligothiophenes containing thienothiadiazole and thienopyrazine central units

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A series of π -conjugated A–D–A–D–A-type oligothiophenes (1–3) comprising heterocyclic thieno[3,4-*c*][1,2,5]thiadiazole (TTDA) or thieno[3,4-*b*]pyrazine (TP) as the core and dicyanovinyl (DCV) or trifluoroacetyl (TFA) as terminal acceptor groups have been developed as red/near-IR absorbers. The resulting oligomers were characterized by UV-Vis spectroscopy, cyclic voltammetry and thermal analysis. The low energy absorption band of these oligomers was located at 620–707 nm in solution and at 695–830 nm in thin films. Theoretical studies reveal that the insertion of the bicyclic nonclassical thiophenes to the conjugated backbone imposed partial quinoidal character to the resulting oligomers and thus reduced the band gap. HOMO–LUMO energies of 1–3 derived from electrochemical measurements were found to be suitable for the use as donor material in combination with fullerene-C₆₀ as acceptor in planar heterojunction solar cells prepared by vacuum deposition. Such devices incorporating these low band gap oligomers exhibited high FF values up to 0.60, and power conversion efficiencies of up to 1.3% under air mass (AM) 1.5G illumination. External quantum efficiency (EQE) spectra clearly showed the contribution of the low energy absorption to the overall photocurrent.

Introduction

During the last decade, the field of organic photovoltaics has seen a remarkable development from syntheses to device performance¹⁻³ and provides bright prospects for the construction of low cost, lightweight and flexible energy sources. In particular, intensive research on small molecule organic solar cells (SMOSCs) has been achieved resulting in a remarkable improvement of the device performance by judicious molecular design, morphology control and device optimization.4-7 Currently, SMOSCs prepared by vacuum processing achieve power conversion efficiencies (PCEs) of up to 8.3% using dicyanovinylene (DCV)-substituted oligothiophenes (DCVnT) as donors and fullerene-C₆₀ as an acceptor.⁸ Various donoracceptor-substituted oligothiophenes have been developed as light-harvesting p-type semiconductors due to their good thermal stability which allows application of vacuum processing as an effective method for controlling the nano-scale morphology of thin films, thus improving the device performance.9-17 Planar heterojunction (PHJ) solar cells based on DCV5T/C60 have been reported with photovoltages as high as 1.0 V and PCEs of up to 4%.9,11,18 Very recently, the PCE has been improved to 5.2% in

bulk heterojunction (BHJ) solar cells prepared by co-evaporation of a non-alkylated **DCV5T** as donor and C_{60} as acceptor.¹⁵

In order to cover an additional part of the solar emission spectrum and thus harvest more incident photons, it is advantageous to design compounds with strong absorptions in the visible and near-infrared (NIR) region. Approaches towards such low band gap materials are the use of strong donoracceptor push-pull systems or the incorporation of o-quinoidal heterocycles in conjugated systems.^{19,20} In this respect, various low band gap oligomers and polymers comprising proquinoid acceptor units such as thienothiadiazole (TTDA)²¹⁻²³ or thienopyrazine (TP)^{22,24-26} have been reported.²⁷⁻²⁹ While TP proved to be an excellent building block for the development of such materials,^{26,30-40} the chemistry and application of nonclassical bicyclic thieno[3,4-c][1,2,5]thiadiazole (TTDA) have not yet been explored in detail.^{21–23,41} In 1969, Bower and Schlessinger first reported the synthesis of a phenyl-capped TTDA unit by reaction of 3,4-dibenzoyl-1,2,5-thiadiazole with phosphorus pentasulfide, showing the longest absorption band at 558 nm in dichloromethane.⁴² Later in 1993, Tanaka and Yamashita synthesized a thiophene-substituted TTDA unit which absorbed at 618 nm in solution, resulting in a small band gap of 2.0 eV, being further reduced to only 0.9 eV ($\lambda_{max} = 934$ nm) in the corresponding polymer.^{21–23} The design of π -conjugated oligomers or polymers containing electron-accepting fused-ring systems in the main chain leads to a strongly enforced quinoidal character of the ground state concomitant with a reduced band gap. Application

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of such narrow band gap polythiophene containing TTDA units in combination with the fullerene derivative $PC_{61}BM$ in solutionprocessed BHJ solar cells gave a very low PCE of only 0.1%.⁴³ Very recently, Mikroyannidis *et al.* reported a PCE of 1.2% for TTDA-containing oligomers as donors and $PC_{61}BM$ as acceptor.⁴⁴ Various TP containing polymers have been used as donors in OSCs with $PC_{61}BM$ or $PC_{71}BM$ as acceptor, showing a PCE of 0.5 to 1.5%.^{38,39,45-48} However, oligomers including a TP-moiety for OSCs have not been reported.

The objective of this study is to shift the absorption of oligothiophenes to the NIR region by insertion of TTDA or TP units as additional electron-accepting core moieties into the main chain. Dicyanovinyl (DCV) and trifluoroacetyl (TFA) groups are applied as terminal acceptor groups in order to tune the thermal and electro-optical properties and to assess useful information about structure-property relationships of the resulting A–D–A– D–A oligomers. Quantum chemical calculations will be used as a guide for the analysis of the electronic spectra and to derive molecular parameters such as ground-state geometry and the electron density distribution. The application of these materials in m-i-p (metal-intrinsic-p-doped)-type planar heterojunction solar cells prepared by vacuum processing is described.

Results and discussion

Synthesis

A Stille-type cross-coupling reaction of stannylated diethylthiophene 4 (ref. 16) and 2,5-dibromo-3,4-dinitrothiophene⁴⁹ using Pd(PPh₃)₄ as catalyst in dry THF gave dinitroterthiophene 5 in 81% yield (Scheme 1). Reduction of the nitro groups in 5 by SnCl₂/EtOH or Pd/hydrogen was found to be difficult, resulting in low conversion yields. Finally, transformation of 5 to 3',4'diaminoterthiophene 6 was performed by Pd/C and hydrazine hydrate in ethanol (88% yield) and due to its low stability it was used without further purification. Reaction of amine **6** with thionylaniline and trimethylsilyl chloride in pyridine afforded trimeric thienothiadiazole **7** in a yield of 70%.

Bromination of terthiophene 7 using NBS followed by a Stilletype cross-coupling reaction with 2-stannylthiophene afforded TTDA-containing pentamer 9 in 72% yield (Scheme 1). Vilsmeier–Haack formylation of quinquethiophene 9 afforded bisaldehyde 10 in a yield of 33%. The use of excess formylating reagent or prolonged reaction time did not improve the product yield. Knoevenagel condensation of dialdehyde 10 with malononitrile and piperidine in 1,2-dichloroethane gave the target A– D–A–D–A oligothiophene 1 in a yield of 87%.

We further introduced TFA acceptor moieties at quinquethiophene 9 in order to study the influence of fluorine substituents on the thermal stability and device performance. TFAsubstituted TTDA-pentamer 2 was prepared in 65% yield by reaction of quinquethiophene 9 with trifluoroacetic anhydride under microwave irradiation (Scheme 1).

Synthesis of DCV-terminated thienopyrazine (TP) oligomer **3** is outlined in Scheme 2. Twofold thiophene-substituted thieno [3,4-b]pyrazine **11** was obtained in 68% yield by condensation of diaminoterthiophene **6** with benzile in methanol. Bromination of **11** using NBS in chloroform and acetic acid afforded trimer **12** in 85% yield. Boronic ester **14** as a coupling reagent was prepared in 87% yield by protection of thiophene-2-carbaldehyde as dioxolane (**13**, 63% yield),⁵⁰ followed by lithiation and subsequent quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane at -78 °C. Suzuki-type cross-coupling reaction of dibromoterthiophene **12** and boronic ester **14** gave quinque-thiophene **15** in 89% yield. The dioxolane groups were deprotected by using catalytic amount of *p*-toluenesulfonic acid in THF and water affording dialdehyde **16** in 54%. Finally, Knoevenagel condensation of pentamer **16** with malononitrile in



Scheme 1 (a) Pd(PPh₃)₄, THF, reflux, 3 d, 81%; (b) hydrazine hydrate, Pd/C (10%), ethanol, rt, 1 h, 88%; (c) TMS-chloride, pyridine, rt, 1 h, 70%; (d) NBS, DCM, 0 °C to rt, 1 d, 92%; (e) 2-(tributylstannyl)thiophene, Pd₂dba₃.CHCl₃, tri-2-furylphosphine, THF, reflux, 3 d, 72%; (f) DMF, POCl₃, 1,2-dichloroethane, reflux, 4 h, 32%; (g) malononitrile, piperidine, 1,2-dichloroethane, reflux, 1.5 h, 87%; and (h) trifluoroacetic anhydride, 1,2-dichloroethane, microwave, 120 °C, 4 h, 65%.



Scheme 2 (a) Benzile, methanol, 60 °C, 4 h, 68%; (b) NBS, acetic acid, chloroform, 2 h, rt, 85%; (c) 14, Pd_2dba_3 .CHCl₃, HP('Bu)₃BF₄, THF/water (4 : 1), sodium phosphate, 100 °C, 1 h, microwave, 89%; (d) *p*-toluenesulfonic acid, THF/water, rt, 24 h, 54%; (e) malonitrile, piperidine, 1,2-dichloroethane, rt, 4–6 h, 66%; (f) *p*-toluenesulfonic acid, toluene, glycol, Dean–Stark apparatus, reflux, 3 h, 63%; and (g): (1) *n*-BuLi, THF, -78 °C, 1 h; (2) ITDB, THF, -78 °C—rt, 1 h, 87%.

the presence of piperidine furnished DCV-substituted TP-oligomer 3 in 66% yield. All compounds were fully characterized by different spectroscopic techniques and elemental analysis.

Thermal properties

The thermal stability of organic materials is one of the important parameters for device fabrication. Therefore, thermal properties of 1-3 were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under an inert atmosphere at a heating rate of 10 °C min⁻¹ as depicted in Fig. 1. TGA analysis revealed that the onset temperatures with 5% weight loss (T_d) of 1, 2 and 3 are 312, 324 and 365 °C, respectively. This result indicates that the thermal stability of the oligomers could be critical for the vacuum processing during device fabrication. DCV-substituted TTDA-derivative 1 showed a moderate sublimation yield ($\sim 20\%$) since during the sublimation process most of the material was decomposed. To overcome this thermal instability, the DCV groups were replaced with TFA units in TTDA-pentamer 2 to lower the sublimation temperature and hence reduce thermal decomposition.51 The melting temperatures (T_m) of 1-3 determined by DSC were 306, 240 and 341 °C, respectively. In DSC, DCV-oligomers 1 and 3 showed a strong exothermic peak immediately after melting, while no such behavior was observed for TFA derivative 2. It has been reported in the literature that the non-classical TTDA heterocyclic unit undergoes an intermolecular Diels-Alder reaction with various dienophiles at high temperature.42,52,53 However, we

were not able to assign the follow-up products of 1 and 3 after melting on the basis of NMR spectral analysis. Thus, we suspect that the compounds reacted in the melt and underwent decomposition.

Spectroscopic studies

Pentamer **9** incorporating a TTDA unit showed the lowest energy absorption maximum at 666 nm with two additional bands at 313 and 390 nm (Fig. 2). The higher energy absorption bands could be correlated to the extended π -conjugative path in the quinquethiophene backbone ($\lambda_{max} = 384$ nm). The insertion



Fig. 2 UV-Vis spectra of compounds 9, 10 and 16 measured in dichloromethane solution.



Fig. 1 (a) TGA thermograms of oligomers 1–3 measured under N₂. Conditions: N₂ flow, 50 ml min⁻¹; heating rate, 10 °C min⁻¹. (b) DSC trace of all derivatives measured under Ar flow at a heating rate of 10 °C min⁻¹.

of aldehyde units does not significantly affect the lowest energy absorption band of **10** (669 nm), while, due to the electron accepting character of the aldehyde groups and extension of the conjugated π -system, a 57 nm red-shift was observed for the higher energy absorption band of **10** (447 nm). Similarly, aldehyde functionalized TP oligomer **16** showed the lowest energy absorption maximum at 573 nm with two additional bands at 395 and 338 nm. The lowest energy absorption maximum of **10** is 96 nm red-shifted compared to that of **16**, suggesting that the TTDA unit is a stronger electron acceptor than TP.

Fig. 3 depicts absorption spectra of oligomers 1-3 measured in dichloromethane and in thin films and the data are summarized in Table 1. Transformation of the aldehyde groups to dicyanovinyl (DCV) in 1 and 3 further red-shifted the lowest energy absorption band to 707 nm for 1 and 620 nm for 3, ascribed to the stronger electron accepting character of the DCV groups. On the other hand, a smaller red-shift was observed for the trifluoroacetyl-substituted pentamer 2 ($\lambda_{max} = 675$ nm), when compared to oligomer 9 or dialdehyde 10. The absorption spectra of 1-3 covered the entire visible spectral region extending from 300 up to 850 nm. In comparison to **DCV5T**^{9,14} ($\lambda_{max} = 507$ nm, $\varepsilon = 51\ 000\ L\ mol^{-1}\ cm^{-1}$), pentamers 1–3 incorporating TTDA or TP units showed a strong red-shift of the longest wavelength absorption band, while the molar extinction coefficients of 1-3 were lowered by a factor of nearly two. The lowest energy absorption maximum of oligomer 1 was red-shifted by 32 nm relative to that of 2 and 88 nm to that of TP-based oligomer 3. The optical absorption data reveal that these oligomers are characterized by a small HOMO-LUMO separation, which could be the result of a significant degree of intramolecular charge transfer from the thienyl donors to the central electron accepting TTDA or TP unit. Furthermore, the high-energy

absorption transitions between 300 and 520 nm can be assigned to multiple excitations arising from the combination of the D–A chromophore in the main π -conjugated chain. In solution, the optical band gaps (E_g^{opt}) for **1–3** estimated from the low energy absorption onset were 1.47, 1.54 and 1.59 eV, respectively, which are significantly lower than that of **DCV5T** (~2.0 eV).^{9,14,15}

The absorption spectrum of oligomer 1 in thin films was extended to over 950 nm with a maximum at 830 nm (Fig. 3b). In addition, the second broad absorption band at 512 nm in the solid state was more intense than in the solution spectrum (516 nm). However, the absorption maximum of TFA derivative 2 in thin films was red-shifted by only 23 nm relative to that obtained in solution. This smaller red-shift of the low energy absorption band of 2 in thin films was rationalized with the weaker acceptor strength of the terminal TFA units relative to that of the DCV groups in oligomer 1. In thin films, TP-oligomer 3 showed an absorption maximum at 700 nm with an onset extending beyond 850 nm. The strong bathochromic shifts of the low energy absorption bands of 1 and 3 in thin films compared to the solution spectra are likely due to strong intermolecular π - π stacking in the solid state. Here it should be noted that the strong red-shift ($\Delta \lambda = 130$ nm) of the low energy absorption band of oligomer 1 compared to that of 3 is due to the stronger acceptor strength of the central TTDA unit compared to the TP moiety. The optical band gaps of these oligomers in thin films are in the range of 1.2 to 1.4 eV.

We noted light-induced photodegradation of thienopyrazine **3** and further studied this process. It has been demonstrated that thienopyrazine-substituted compounds rapidly degrade when exposed to UV light and air at the same time and was speculated to the possible cleavage of C=N double bonds.⁵⁴ Fig. 4 depicts the UV-Vis absorption spectra of **3** in dichloromethane solution



Fig. 3 Absorption spectra of compounds 1-3 in (a) solution and in (b) solid state, 30 nm thin films prepared by vacuum evaporation.

Table 1	UV-Vis data of	title compounds	1–3 in	dichloromethane	solution	$([c] = 10^{-5})$	' M)
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Compound	λ_{abs}/nm sol.	$\varepsilon^{a}/L \text{ mol}^{-1} \text{ cm}^{-1}$	E_{g}^{opt}/eV sol.	λ_{abs}/nm film	E_{g}^{opt} /eV film
9	313, 390, 666	14 400	1.52		
10	313, 447, 669	20 600	1.52		
16	338, 395, 573	16 100	1.73		
1	319, 362, 458 (sh), 516, 707	29 000	1.47	512, 830	1.20
2	317, 408 (sh), 483, 675	30 000	1.54	514, 698	1.39
3	358, 512 (sh), 620	31 000	1.59	700	1.39
DCV5T ^b	506	51 100	2.04	569	1.76

^a The molar extinction coefficient values are given for the longest wavelength absorption band. ^b Values taken from ref. 14.



Fig. 4 Absorption spectra of compound 3 in (a) dichloromethane solution ($[c] = 10^{-5} \text{ mol} \cdot L^{-1}$) and in (b) solid state, 10 nm thin film prepared by vacuum evaporation.

and in thin films recorded over time when exposed to air and sunlight.

When exposed to sunlight under ambient atmosphere, the longest wavelength absorption of 3 at 620 nm rapidly decreased in solution, while a new absorption band appeared with a maximum at 420 nm. After 12 hours of irradiation this transformation was completed (Fig. 4a). In the solid state and in the absence of oxygen, no change in absorption was observed after one hour of sunlight irradiation. After exposure to ambient atmosphere, degradation was observed, yet in a significantly lower rate than in solution. In addition, the change in the absorption profile in the solid state is characterized by a moderate decrease of the longest wavelength absorption together with slight broadening of the absorption band in the region from 350 to 500 nm and an additional absorption at around 460 nm, which would correspond to the new band at 420 nm in solution (Fig. 4a). MALDI-TOF and ¹H-NMR analyses of 3 after light exposure showed multiple peaks due to photodegradation which could not be unequivocally assigned to possible follow-up products.

Electrochemical characterization

Fig. 5 depicts cyclic voltammograms of oligomers 1-3 measured in dichloromethane solution containing 0.1 M TBAPF₆ as supporting electrolyte. The electrochemical data are summarized in Table 2. Pentamer 9 showed a reversible one-electron reduction associated with the TTDA unit and two reversible one-electron oxidation processes for the oligothiophene backbone (Fig. 5a). The introduction of the aldehyde groups in **10** resulted in a slight positive shift of the oxidation potentials ($\Delta E_{ox} = 90$ and 130 mV) when compared to **9** and the appearance of a second reduction wave at -1.66 V related to the electron accepting aldehyde groups. The replacement of the TTDA unit by TP in **16** has no influence on the oxidation potential, while the reduction potentials shifted to more negative values ($\Delta E_{ox} = 250$ and 100 mV). This negative shift in the reduction potentials further supports the weaker acceptor strength of TP when compared to the TTDA unit.

The investigated compounds **1–3** each showed two fully reversible one-electron oxidation waves, which can be assigned to the oxidation of the oligothiophene backbone. At cathodic potentials, we observed a reversible wave between -1.2 and -1.36 V (*vs.* Fc/Fc⁺) corresponding to a two-electron reduction of the TTDA/TP units and a quasi-reversible reduction wave between -1.86 and -2.08 V associated with the one-electron reduction of the DCV and TFA groups, respectively. The results indicate the formation of stable radical cations, dications, radical anions, and dianions. Compared to **DCV5T**, a negative shift of the oxidation waves and a positive shift of the reduction waves were observed for these new oligomers.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of all oligomers were determined from the onset values of the first oxidation and reduction waves using the standard approximation that the Fc/ Fc⁺ HOMO energy level is at -5.1 eV vs. vacuum.⁵⁵ These data are listed in Table 2. The low band gap materials **1–3** studied here showed strong positive shifts of the reduction potentials and



Fig. 5 Cyclic voltammogram of TTDA derivatives 9, 10 and TP derivative 16 (a) and of pentamers 1, 2 and 3 (b) $(1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1})$ in DCM/TBAPF6 (0.1 M).

Compound	$E^{\circ}_{\rm Ox1}/{\rm V}$	$E^{\circ}_{\rm Ox2}/{\rm V}$	$E^{\circ}_{\rm Red1}/{\rm V}$	$E^{\circ}_{\text{Red2}}/\text{V}$	HOMO/eV	LUMO/eV	$E_{\rm g}/{\rm eV}$
9	0.23	0.56	-1.35		-5.24	-3.84	1.40
10	0.32	0.69	-1.37	-1.66	-5.34	-3.83	1.51
16	0.34	0.69	-1.62	-1.76	-5.38	-3.59	1.79
1	0.35	0.73	-1.21	-1.91	-5.39	-3.94	1.45
2	0.39	0.78	-1.33	-2.08	-5.41	-3.88	1.53
3	0.36	0.71	-1.36	-1.86	-5.36	-3.83	1.53
DCV5T ^a	0.59	0.88	-1.51	-1.98	-5.62	-3.75	1.87

Table 2 Summarized cyclovoltammetry data of title compounds 1–3 measured in DCM (HOMO/LUMO vs. $Fc/Fc^+_{vac} = -5.1 \text{ eV}$)

consequently lower LUMO energy levels compared to those of **DCV5T**, demonstrating that the TTDA/TP units behave as strong electron acceptors. It has been reported that upon attachment of electron-withdrawing moieties at the terminal α -positions of linear π -conjugated chains, the relative HOMO and LUMO energies shift toward lower energy values with respect to the unsubstituted system. The LUMO energies are more affected than those of the HOMOs and thus the band gaps are low-ered.^{15,56} However, the determined orbital energies for 1–3 revealed a different trend. The insertion of *o*-quinoidal TTDA/TP units in the core of an oligomer stabilizes the LUMO, but destabilizes the HOMO energy at the same time, thus reducing the band gap to a large extent relative to **DCV5T** (Fig. 6). The low-lying LUMO energies of these oligomers could lead to problems in electron transfer to C₆₀.

The ground-state geometry and the electron density distribution of the HOMO and LUMO of 1–3 have been fully optimized using density functional theory (DFT) (B3LYP 6-31G*) and semi-empirical methods (Austin Model 1, AM1). The MO distributions of the frontier orbitals from the latter method are shown in Fig. 7 including **DCV5T** for comparison. It has been hypothesized that the band gap of a conjugated system can be reduced either by incorporation of suitable donor and acceptor units or by lowering the degree of bond-length alternation (BLA) (defined as the difference between average lengths of C–C single and double bonds in a conjugated path).^{58,59} It has also been proposed that the introduction of appropriate quinoid structures into the aromatic backbone can minimize the BLA and may



Fig. 6 HOMO–LUMO energy levels of the investigated oligomers 1–3 deduced from electrochemical data and compared to C_{60} . The HOMO and LUMO energy values of C_{60} estimated from the onset of the oxidation and reduction potentials are taken from ref. 57.



Fig. 7 Electron density distribution of the frontier orbitals in derivatives 1–3 and DCV5T obtained from quantum chemical calculations (carbon atoms in black, fluorine in light blue, nitrogen in blue, oxygen in red, sulfur in yellow and hydrogen atoms are omitted for clarity reasons).

reduce the band gap accordingly.^{58,60,61} The increasing doublebond character between the repeating units of a conjugated system can be accomplished by making the quinoidal structure energetically more favorable.

Yamashita and co-workers reported that after the substitution of the conjugated systems by terminal acceptor units⁵⁶ or by attaching nonclassical heterocyclic cores,23,62 the aromatic character of the backbone changes to a partially quinoid-like character in which the degree of BLA was significantly reduced. The semiempirical analysis of the overall BLA for oligomers 1-3 revealed a strong reduction from aromatic quinquethiophene (0.039 Å) to **DCV5T** (0.032 Å) to a value of 0.021 Å for 1 and 2 and 0.023 for 3. Thus, the bicyclic nonclassical thiophene imposes a partial quinoidal character to the conjugated backbone, leading to a more delocalized molecular structure. The same trend is obtained from DFT calculations. The decrease of BLA can be directly correlated to the influence of, on the one hand, the TTDA/TP acceptor moiety and, on the other hand, the terminal acceptor groups on the extended π -system of the molecules and is the origin of the red-shifted absorption band (vide supra). The electron density of the HOMO for all molecules is distributed not only on the oligothiophene backbone, but also on the central TTDA/TP-acceptor moiety, while that of the LUMO is mainly localized on the central acceptor units and the adjacent thiophene rings. The phenyl rings attached to pyrazine in 3 are strongly twisted out of plane, hence do not contribute to the frontier molecular orbital distribution. Although the delocalization of the exciton can be favored by the decrease in BLA in 1-3, the localization of the electron density on the central TTDA/TP unit in the excited state (LUMO) could act as a trap for excitons. This could further affect the device performance (*vide infra*).

Solar cell performance

The HOMO/LUMO energy levels of some of these low band gap oligomers are suitable for the application of these materials as donors in organic solar cells when using C_{60} as electron acceptor. As the compounds are stable in the solid state, m-i-p-type planar heterojunction (PHJ) solar cells were fabricated by vacuum evaporation. Fig. 8 shows J-V curves of SMOSCs using 6 nm thick layers of 1-3 as donors and C₆₀ as an acceptor. The device structure with optimized layer sequences consisted of ITO/C₆₀ (15 nm)/1-3 (6 nm)/Di-NPB (5 nm)/Di-NPB:NDP9 (40 nm, 5 wt %)/ZnPc:NDP9 (10 nm, 3 wt%)/Au (50 nm). By using these highly optimized device structures, it enables us to investigate the effect of the donor/active layer on power conversion efficiencies. In these device structures the hole transport layers (HTLs) have to be chosen in order to match the energy levels of the active layers with the Fermi level of the metal electrodes. By using pdoped HTL N,N'-diphenyl-N,N'-bis(4'-(N,N-bis(naphth-1-yl)amino)-biphenyl-4-yl)-benzidine (Di-NPB) we can adjust the HOMO of the HTL to the HOMO of the donor materials (oligomers 1-3), avoiding energetic barriers and assuring a good hole transport (due to the doping). For p-doping, NPD9 (Novaled AG, Dresden) was used between the HTL and the Au top electrode, to facilitate charge extraction. The intrinsic HTL was introduced to avoid direct contact between the active layer and the doped HTL that otherwise could lead to quenching of excitons by the dopants. Furthermore, by using p-doped ZnPc we assure a good ohmic contact to the Au top electrode. Thus, we can really analyze the influence of the donor material at the C_{60} interface in a device that is highly reproducible and with energetically adjusted HOMO levels. Table 3 presents the photovoltaic data of the corresponding devices.

All compounds showed moderate short-circuit current density (J_{SC}) values between 2.6 and 3.2 mA cm⁻². This could be ascribed to the lack of transport of the photo-generated electrons and holes at the D–A interface, resulting in significant recombination

Table 3Characteristic photovoltaic data of m-i-p-type planar hetero-
junction solar cells of 1–3 in full sunlight (AM 1.5G, 100 mW cm $^{-2}$)

Compound	V _{OC} /mV	J _{SC} /mA cm ⁻²	FF	η (%)
1	0.70	2.76	0.43	0.8
2	0.77	2.89	0.48	1.1
3	0.68	3.20	0.60	1.3

and low values of J_{SC} and FF. It should be noted that the FF value obtained with oligomer 3-based devices (FF = 0.60) is among the highest values reported for small molecule solar cells. All the studied materials displayed as well moderate $V_{\rm oc}$ values in the range of 0.68 to 0.77 V. This is due to the fact that $V_{\rm OC}$ is limited by the difference between the HOMO energy level of the donor and the LUMO energy level of the acceptor,63,64 restricting the overall device efficiencies (η) , which were determined to be 0.8, 1.1 and 1.3% for oligomers 1-3, respectively. To ensure an efficient charge separation, it has been suggested that a minimum LUMO(D)-LUMO(A) offset of about 0.3-0.4 eV is necessary.^{38,64} The difference between the LUMO of these oligomers and the LUMO of C₆₀ is only about 0.27-0.16 eV (obtained from Fig. 6), which indeed appears to be insufficient for efficient electron transfer at the donor/acceptor interface from the excited state of these low band gap oligomers. Therefore, only a small fraction of the absorbed photons could be dissociated into charge carriers that can reach the electrodes under influence of the internal electric field. Fig. 8b shows the external quantum efficiency (EQE) spectra of devices based on pentamers 1, 2 and 3. Compounds 2 and 3 display broad EQE spectra covering from 400 up to 850 nm region, which is extended up to 900 nm for oligomer 1. The result is also consistent with their absorption spectrum in thin films, thus showing the contribution of the CTband to the EQE and J_{SC} . The lower J_{SC} values obtained with these devices are also in good agreement with the lower molar extinction coefficients of oligomers 1-3 and low EQEs over the entire visible light region.

Conclusions



We have developed novel conjugated A–D–A–D–A-type oligothiophenes with thienothiadiazole/thienopyrazine as core and dicyanovinylene/trifluoroacetyl as terminal acceptor units. The

Fig. 8 (a) J-V characteristics of m-i-p-type planar heterojunction solar cells under standard AM 1.5G conditions (100 mW cm⁻²). (b) EQE spectra of pentamers 1 and 3.

obtained materials showed strong absorption down to the near IR-region with narrow band gaps down to 1.5 eV in solution and about 1.2 eV in thin films. All compounds showed broad absorption bands ranging from 300 to 850 nm. Substitution of dicyanovinyl units with electron withdrawing trifluoroacetyl groups resulted in a highly stable compound, thus reducing the thermal decomposition of the material during vacuum sublimation. The insertion of TTDA/TP units reduces the bond length alternation along the π -conjugated backbone and leads to a more delocalized *i.e.* partially quinoidal character. The results show that the lowering of the band gap in these A-D-A-D-A systems with respect to the standard DCV5T comes not only from the partial stabilization of the LUMO energy but also from a similar destabilization of the HOMO energy. Despite their low molar extinction coefficients, m-i-p-type photovoltaic devices based on the new materials as donors with fullerene-C₆₀ as the acceptor showed a high fill factor of up to 0.60 and power conversion efficiencies (PCE) in the range of 0.8 to 1.3%. The values reported here represent one of the best performances among low-band gap conjugated small molecules. The obtained PCEs can be explained in part due to the lower molar extinction coefficients of these oligomers and to the low-lying LUMO energy levels of the donor, which provides an insufficient driving force for electron transfer from the LUMO of the donor to the LUMO of the acceptor. Increasing the molar absorptivity in the low energy region by attaching suitable building blocks and at the same time maintaining appropriate HOMO/LUMO energy levels might be a possible way to obtain better J_{SC} and efficiency values, and work to this end is in progress in our laboratory.

Experimental

Instrumentations. NMR spectra were recorded on a Bruker AMX 500 (1H NMR: 500 MHz, 13C NMR: 125 MHz) or an Avance 400 spectrometer (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz), unless mentioned otherwise at 25 °C. Chemical shift values (δ) are expressed in parts per million using residual solvent protons (¹H NMR, $\delta_{\rm H} = 7.26$ for CDCl₃, $\delta_{\rm H} = 5.32$ for CD₂Cl₂, $\delta_{\rm H} = 5.93$ for CD₂Cl₄; ¹³C NMR, $\delta_{\rm C} = 77.0$ for CDCl₃, $\delta_{\rm C} = 53.8$ for CD_2Cl_2 , $\delta_C = 74.2$ for CD_2Cl_4) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet) and m (multiplet). The assignments are Ar-H (H-atoms of aromatic systems) and Th-H (H-atoms of thiophene rings). Melting points were determined using a Büchi B-545 apparatus and were not corrected. Elemental analyses were performed on an Elementar Vario EL (University of Ulm) and a Carlo Erba 1104 (University of Stuttgart). Thin layer chromatography was carried out on aluminium plates, pre-coated with silica gel, Merck Si60 F₂₅₄. Preparative column chromatography was performed on glass columns packed with silica gel, Merck Silica 60, particle size 40-43 µm. CI and EI mass spectra were recorded on a Finnigan MAT SSQ-7000 or a Varian Saturn 2000 GC-MS, MALDI-TOF on a Bruker Daltonics Reflex III. UV/Vis absorption spectra were recorded in 1 cm cuvettes with Merck Uvasol grade solvents on a Perkin Elmer Lambda 19 spectrometer. Cyclic voltammetry experiments were performed with a computer-controlled Autolab PGSTAT30 potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode, and an Ag/ AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferrocenium couple. Tetrahydrofurane (*Merck*) was dried under reflux over sodium/benzophenone (*Merck*) and dichloromethane (*Merck*) over calcium hydride (*Merck*). All synthetic steps were carried out under argon atmosphere. *N*-Bromo succinimide (NBS), NaOH and K₂CO₃ were purchased from *Merck*, Pd(PPh₃)₂Cl₂, trifurylphosphine (TFP) and *n*BuLi (1.6 mol L⁻¹ in hexane) from *Acros*, tri-*n*butyltin chloride and tri-*n*-methyltin chloride from *Aldrich*. Hyperchem (Austin Model 1) and Gaussian 09 (AM1 and B3LYP/6-31G*) software were used to perform the geometry optimization for all oligomers.

Solar cell fabrications. N, N'-Di(naphthalen-1-yl)-N, N'diphenyl-benzidine (Di-NPB) and zinc phthalocyanine (ZnPc), doped with proprietary compounds NDP2 or NDP9 of Novaled GmbH (Dresden), were used as p-doped hole transport layers. Doping concentrations of Di-NPB and ZnPc were 2-5 wt%. C₆₀ and ZnPc have been provided by Alfa Aesar and Di-NPB by Sensient Imaging Technologies. Except the oligothiophenes, all materials were cleaned at least twice by thermal gradient sublimation before evaporation. The organic layers and metal contacts were thermally deposited in an ultra high vacuum system ("UFO", Bestec GmbH) at 10^{-8} to 10^{-7} mbar through shadow masks onto semitransparent indium tin oxide (ITO) coated glass substrates (Thin Film Devices Inc., sheet resistance < 30 Ω sq⁻¹) without breaking the vacuum. Ceramic or graphite crucibles were used as sublimation sources (Creaphys GmbH, Reinhardtsgrimma), temperatures were set by a Eurotherm controller and film thicknesses were determined by quartz crystal monitors (Leybold Inficon Inc.). Substrates were cleaned using detergent, acetone, and ethanol. The active area of the solar cells was 6.4 mm². In order to precisely determine the solar cell efficiencies, all three cells were measured with an aperture mask of 2.76 mm². J-V characteristics were measured using a Source measurement Unit (Keithley SMU 236) in an N2-filled glovebox without exposing the samples to air. Illumination was provided by a sun simulator SOL 1200 (Hoehnle) with an intensity of 127 mW cm⁻², which was calibrated using an outdoor reference cell provided by the Fraunhofer Institute for Solar Energy Systems (Freiburg). The mismatch between the spectrum of our sun simulator and the AM1.5 spectrum was taken into account when calculating the power conversion efficiencies of the solar cells. External quantum efficiency (EQE) spectra were recorded using a custom-made setup utilizing a xenon arc lamp, a monochromator (Newport Cornerstone) and a lock-in amplifier (Signal Recovery 7265 DSP). A silicon reference diode (Hamamatsu S1337) was used to calibrate the setup. Organic films for spectral analysis were vapor deposited onto quartz substrates under ultra high vacuum with deposition rates of about 0.1 Å s^{-1} . A commercial Shimadzu UV-2101/3101 spectrophotometer was used for absorption measurements. Luminescence spectra were recorded using a Spex FluoroMAX with separated monochromators for excitation and luminescence light.

3,4:3",**4**"-**Tetraethyl-3**'**4**'-**dinitro-2,2**':**5**',**2**"-**terthiophene (5).** To a solution of 2,5-dibromo-3,4-dinitrothiophene (10.0 g, 30.2 mmol) in absolute THF (200 ml) under argon atmosphere were added tributyl-(3,4-diethyl-thien-2-yl)-stannane (**4**) (31.0 g,

72.2 mmol) and Pd(Ph₃)₄ (346 mg, 0.30 mmol). After refluxing for 3 h, a second portion of catalyst (346 mg) was added and the reaction mixture was refluxed for another 19 h. The solvent was evaporated to a large extent and the raw product was precipitated by addition of *n*-hexane. Subsequent recrystallization from ethanol, followed by column chromatography (SiO₂, petroleum ether (40–65 °C)/dichloromethane = 3 : 2 v/v, $R_{\rm f} = 0.25$) afforded 5 (11.08 g, 24.6 mmol) in 81.4% yield as yellow crystals. M.p.: 100–101 °C. ¹H NMR (CDCl₃, TMS, 400 MHz): δ [ppm] = 7.17 (s, 2H, Th-H), 2.61 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 2.60 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 1.31 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃), 1.11 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃). ¹³C NMR (CDCl₃, δ ppm) 146.0, 144.5, 138.5, 135.2, 123.7, 120.5, 22.1, 21.1, 14.6, 13.6; MS (CI): m/z = 450 (M⁺, 40%); 451 (M⁺ + H, 60%). Elemental analysis: $C_{20}H_{22}N_2O_4S_3$: calc. C, 53.31; H, 4.92; N, 6.22%; found C, 53.25; H, 4.89; N, 6.23%.

3,4,3'',4''-Tetraethyl-3'4'-diamino-2,2':5'',2''-terthiophene (6). To a suspension of ground 3,4:3",4"-tetraethyl-3',4'-dinitro-2,2':5',2"-terthiophene 5 (0.90 g, 2.0 mmol) in ethanol (16 ml) under argon atmosphere were added Pd/C (0.45 g, 10% Pd by weight) and hydrazine monohydrate (10.0 g, 200 mmol). After stirring for 2 h, the Pd/C catalyst was removed by filtration through a Celite pad and washed with dichloromethane (caution: dry catalyst is pyrophorous). The organic phase was washed with aqueous ammonium chloride, saturated aqueous sodium bicarbonate solution and water. The organic phase was then dried $(MgSO_4)$, filtered, and concentrated by a rotary evaporator. The crude product was column chromatographed (SiO₂, n-hexane/ THF = 2 : 1 v/v; $R_f = 0.37$) to yield **6** (691 mg, 1.77 mmol, 88.4%) as a slightly brownish viscous liquid which was pure enough to use without further purification. ¹H NMR (CDCl₃, δ ppm) 6.98 (s, 2H, Th-H), 3.47 (broad s, 4H, NH₂), 2.61 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 2.60 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 1.30 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃), 1.10 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃). ${}^{13}C$ NMR (CDCl₃, δ ppm) 144.3, 144.5, 142.8, 134.5, 128.0, 120.0, 109.4, 22.3, 20.8, 15.0, 13.7. MS (CI): m/z = 390 (M⁺, 55%); 391 (M⁺ + H, 100%). Elemental analysis: C₂₀H₂₆N₂S₃: calc. C, 61.50; H, 6.71; N, 7.17%; found C, 61.60; H, 6.74; N, 7.06%.

4,6-Di-(3,4-diethylthien-2-yl)-thieno[3,4-c][1,2,5]thiadiazole (7). To a stirred solution of 3,4:3",4"-tetraethyl-3',4'-diamino-2,2':5',2"-terthiophene 6 (1.53 g, 3.92 mmol) in dry pyridine (22 ml) under argon atmosphere was added freshly distillated Nthionylaniline (1.09 g, 7.84 mmol, b.p. 77 °C/15 mbar) via a syringe. Then, trimethylsilyl chloride was added (2.98 g, 27.4 mmol), resulting in a dark blue color. After 2 h of stirring at ambient temperature, dichloromethane (250 ml) was added and the solution was washed with 1 N hydrochloric acid $(2 \times 150 \text{ ml})$ and with water. The organic phase was dried over MgSO4 and then the solvent was removed under vacuum, yielding the crude product. The excess of N-thionylaniline was removed by extraction with n-hexane (100 ml). The solid product was filtered and recrystallized from *n*-hexane (300 ml) to give 7 (1.14 g, 2.73 mmol,) in a yield of 70% as a dark blue colored crystal. M.p.: 115 °C. TLC: $R_f = 0.53$ (*n*-hexane/THF = 2:1 v/v), $R_f = 0.74$ (dichloromethane/petroleum ether = 2:1). ¹H NMR (CDCl₃, δ ppm) 7.07 (s, 2H, Th-H), 2.92 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 2.64 $(q, {}^{3}J = 7.5 \text{ Hz}, 4\text{H}, \text{CH}_{2}), 1.32 (t, {}^{3}J = 7.5 \text{ Hz}, 6\text{H}, \text{CH}_{3}), 1.26$ (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃). 13 C NMR (CDCl₃, δ ppm) 156.7, 144.8, 140.4, 128.9, 121.0, 112.9, 22.1, 21.3, 14.0, 13.8. MS (CI): m/z = 418 (M⁺, 51%); 419 (M⁺ + H, 100%). Elemental analysis: C₂₀H₂₂N₂S₄: calc. C, 57.38; H, 5.30; N, 6.69%; found C, 57.43; H, 5.34; N, 6.72%.

4,6-Bis(5-bromo-3,4-diethylthien-2-yl)-thieno[3,4-c][1,2,5]thiadiazole (8). To a solution of terthiophene 7 (654 mg, 1.56 mmol) in DMF (49 ml) was added dropwise a solution of NBS (612 mg, 3.44 mmol) in DMF (33 ml) at 0 °C. The cooling bath was removed and the solution was kept stirring at room temperature until completion of the reaction. The reaction was controlled by TLC using dichloromethane : n-hexane (1 : 1) as eluent. After 5 h of stirring, the mixture was dissolved in dichloromethane (150 ml) and washed with water (3 \times 200 ml). The organic phase was dried over sodium sulfate and the solvent was removed by vacuum. The product was purified by column chromatography (SiO₂, dichloromethane 1 : 1 *n*-hexane) to obtained 8 (818 mg, 1.42 mmol) as deep blue crystals in a yield of 92%. M.p.: 130.5-132 °C. ¹H NMR (CDCl₃, δ ppm) 2.93 (q, ³J = 7.6 Hz, 4H, CH₂), 2.65 (q, ${}^{3}J = 7.6$ Hz, 4H, CH₂), 1.27 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃), 1.20 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃). ${}^{13}C$ NMR (CDCl₃, δ ppm) 156.6, 143.6, 143.2, 140.8, 139.9, 129.2, 22.3, 21.8, 14.3, 14.2. MS (CI): m/z 573.7 [M]⁺ (calc. for C₂₀H₂₀Br₂N₂S₄: 573.9). Elemental analysis: calc. for C₂₀H₂₀Br₂N₂S₄: C, 41.67; H, 3.50; N, 4.86%; found: C, 41.86; H, 3.62; N, 4.84%.

4,6-Bis(3,4-diethyl-2,2'-bithien-5-yl)-thieno[3,4-c][1,2,5]thiadiazole (9). Dibromo-terthiophene 8 (817 mg, 1.42 mmol), tri-2furylphosphine (131.6 mg, 0.57 mmol) and Pd₂(dba)₃·CHCl₃ (73.35 mg, 0.07 mmol) were dissolved in freshly dried THF (140 ml). After stirring at room temperature for 20 min, 2-(tributylstannyl)-thiophene (1.85 g, 4.96 mmol) was added and the mixture was heated up to 60 °C. Stirring was continued at this temperature for two days. After cooling, aqueous ammonium chloride solution was added and the mixture was extracted with dichloromethane (300 ml). The organic phase was dried over sodium sulfate and the solvent was removed under reduced pressure. The product was purified by column chromatography (SiO₂, DCM : *n*-hexane (1 : 1)) to obtain 9 (654 mg, 1.12 mmol) in 79% as deep green powder. M.p.: 196 °C. ¹H NMR (CDCl₃, δ ppm) 7.35 (dd, J = 5.1 Hz and 1.2 Hz, 2H, Th-H^{β}), 7.24 (dd, ³J = 3.6 Hz and 1.1 Hz, 2H, Th-H^{β}), 7.11–7.08 (dd, J = 5.1 Hz and 3.6 Hz, 2H, Th-H^{α}), 3.0 (q, ³J = 7.5 Hz, 4H, CH₂), 2.83 (q, ³J = 7.5 Hz, 4H, CH₂), 1.33 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃), 1.27 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃). ¹³C NMR (CDCl₃, δ ppm) 141.5, 141.2, 135.9, 132.5, 130.2, 128.3, 127.5, 126.6, 126.1, 125.6, 99.9, 21.9, 15.3, 14.2; MS (MALDI): m/z 581.9 [M]⁺ (calc. for C₂₈H₂₆N₂S₆: 582.0). Elemental analysis: calc. for C₂₈H₂₆N₂S₆: C, 57.69; H, 4.50; N, 4.81%; found: C, 57.86; H, 4.69; N, 4.63%.

5',5''-(Thieno[3,4-c][1,2,5]thiadiazol-4,6-diyl)bis(3',4'-diethyl-2,2'-bithiophene-5-carbalde-hyde) (10). Phosphoryl chloride (0.78 ml, 8.50 mmol) and dimethylformamide (0.66 ml, 8.50 mmol) were dissolved in 1,2-dichloroethane (8.5 ml) and stirred at room temperature for two hours. Quinquethiophene 9 (110 mg, 0.19 mmol) was dissolved in 1,2-dichloroethane (6 ml) and the formed Vilsmeier reagent was added. The mixture was stirred under reflux (110–120 °C) for 4 h. After cooling, dichloromethane (80 ml) and aqueous solution of sodium hydrogen carbonate (240 ml) were added. Stirring was continued overnight at room temperature. The organic phase was washed several times with water, dried over sodium sulfate, filtered, and evaporated. Column chromatography with dichloromethane and ethyl acetate (9:1) as the mobile phase afforded compound 10 (40 mg, 0.06 mmol) in a yield of 33%. The corresponding mono-aldehyde was also isolated in a vield of 12%. M.p.: 251 °C. ¹H NMR $(CDCl_3, \delta \text{ ppm})$ 9.91 (s, 2H, OHC), 7.74 (d, ${}^{3}J = 4.0 \text{ Hz}$, 2H, Th-H), 7.37 (d, ${}^{3}J = 4.0$ Hz, 2H, Th-H), 3.03 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 2.91 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 1.35 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃), 1.31 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃). ${}^{13}C$ NMR (CDCl₃, δ ppm) 206.5, 159.9, 157.1, 145.8, 143.6, 142.5, 142.1, 136.7, 131.5, 130.6, 126.4, 21.9, 21.2, 14.9, 14.0. MS (MALDI): m/z 637.7 [M]⁺ (calc. for C₃₀H₂₆N₂O₂S₆: 638.0). Elemental analysis: calc. for C₃₀H₂₆N₂O₂S₆: C, 56.40; H, 4.10; N, 4.38%; found: C, 56.66; H, 4.32; N, 4.11%.

2,2'-(5',5"-(Thieno[3,4-c][1,2,5]thiadiazol-4,6-diyl)bis(3',4'diethyl-2,2'-bithien-5,5'-diyl))bis-(methan-1-yl-1-ylidene)dimalononitrile (1). Bis-aldehyde 10 (30 mg, 0.05 mmol), malononitrile (40 mg, 0.61 mmol) and piperidine (8.0 mg, 0.09 mmol) were dissolved in 1,2-dichloroethane (10 ml) and stirred at room temperature for 1 h. The mixture was then heated up to 70 °C and stirred again for another hour. The reaction was controlled by TLC using dichloromethane and ethyl acetate (9:1) as the mobile phase. After cooling down to room temperature, the solid product was filtered, washed with *n*-hexane and dried under vacuum. Column chromatography on silica using dichloromethane as the solvent afforded 1 (30 mg, 0.04 mmol, 87%) as deep lilac powder. M.p.: 305 °C. ¹H NMR (CD₂Cl₄, 500 MHz, 100 °C) δ ppm: 7.71 (d, ${}^{3}J = 4.2$ Hz, 2H, Th-H), 7.70 (s, 2H, Vinyl-H), 7.36 (d, ${}^{3}J = 4.2$ Hz, 2H, Th-H), 3.01 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 2.90 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 1.33 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃), 1.29 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃). ${}^{13}C$ NMR (CD₂Cl₄, 125 MHz, 100 °C) δ ppm: 157.50, 149.50, 148.16, 145.09, 143.01, 138.56, 134.53, 132.05, 131.14, 126.98, 120.49, 114.33, 113.57, 113.38, 21.94, 21.51, 14.65, 14.02. MS (MALDI): m/z 733.7 [M]⁺ (calc. for C₃₆H₂₆N₆S₆: 734.1). Elemental analysis: calc. for C₃₆H₂₆N₆S₆: C, 58.83; H, 3.57; N, 11.43%; found: C, 58.57; H, 3.58; N, 11.50%.

1,1'-(5',5''-(Thieno[3,4-c][1,2,5]thiadiazol-4,6-diyl)bis(3',4'-diethyl-2,2'-bithien-5,5'-diyl))bis-(2,2,2-trifluoroethanone) (2). To a solution of quinquethiophene 9 (300 mg, 0.51 mmol) in 1,2-dichloroethane (32 ml) was added trifluoroacetic anhydride (21 ml). The mixture was irradiated by microwave for four hours at 120 °C. After completion of the reaction, the solvent was removed under reduced pressure and the product was purified by column chromatography (SiO₂) eluating with pure dichloromethane. Recrystallization, using Soxhlet apparatus with 1,2-dichloroethane as solvent, afforded 2 (259 mg, 0.33 mmol, 65%) as dark brown powder. M.p.: 221 °C. ¹H NMR (CD₂Cl₄, 500 MHz, 100 °C) δ ppm: 7.90-7.85 (m, 2H, Th-H), 7.32 (d, ${}^{3}J = 4.2$ Hz, 2H, Th-H), 2.99 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 2.88 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 1.31 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃), 1.28 $(t, {}^{3}J = 7.5 \text{ Hz}, 6\text{H}, C\text{H}_{3})$. ${}^{13}\text{C}$ NMR $(CD_{2}Cl_{4}, 125 \text{ MHz}, 100 °C)$ δ ppm: 157.5, 144.8, 142.9, 136.8, 134.9, 131.6, 131.1, 127.1, 120.5, 113.3, 21.9, 21.4, 14.8, 14.1. MS (MALDI-TOF): m/z 775.0 [M]+ (calc. for $C_{32}H_{24}F_6N_2O_2S_6$: 774.0). Elemental analysis: calc. (%) for

 $C_{32}H_{24}F_6N_2O_2S_6{:}$ C, 49.60; H, 3.12; N, 3.61%; found: C, 49.66; H, 3.08; N, 3.43%.

5,7-Bis(3,4-diethylthien-2-yl)-2,3-diphenylthieno[3,4-b]pyrazine (11). 3,4,3",4"-Tetraethyl-[2,2';5',2"]terthiophen-3',4'-diamine 6 (4.08 g, 10.4 mmol, 1.0 eq.) and benzile (2.43 g, 11.6 mmol, 1.1 eq.) were dissolved in methanol (250 ml). The mixture was heated up to 70 °C and stirred for 12 h under argon atmosphere. After cooling down, the formed precipitate was filtered off, washed with a small amount of methanol and dried under vacuum. Column chromatography (silica, DCM : n-hexane = 7 : 3) furnished product 11 (4.02 g, 7.1 mmol) as deep red powder in a yield of 68%. M.p.: 168-169 °C. ¹H NMR (CDCl₃, 400 MHz) δ ppm: 7.58–7.54 (m, 4H, Ar-H), 7.37–7.27 (m, 6H, Ar-H), 7.12 (ws, 2H, Th-H), 2.96 (q, ${}^{3}J = 7.6$ Hz, 4H, $-CH_2$), 2.65 (dq, J = 7.5 Hz and 1.0 Hz, 4H, $-CH_2$), 1.33 $(t, {}^{3}J = 7.4 \text{ Hz}, 6\text{H}, C\text{H}_{3}), 1.27 (t, {}^{3}J = 7.5 \text{ Hz}, 6\text{H}, C\text{H}_{3}).$ (CDCl₃, 100 MHz) δ ppm: 152.3, 144.1, 141.2, 139.0, 137.8, 129.9, 128.7, 128.0, 127.8, 125.4, 121.8, 22.0, 21.3, 14.4, 13.8. MS (MALDI-TOF): m/z 564.2 [M]⁺ (calc. for C₃₄H₃₂N₂S₃: 564.2). Elemental analysis: calc. (%) for C₃₄H₃₂N₂S₃: C, 72.30; H, 5.71; N, 4.96; found: C, 72.10; H, 5.77; N, 4.83.

5,7-Bis(5-bromo-3,4-diethylthien-2-yl)-2,3-diphenylthieno[3,4b|pyrazine (12). Thienopyrazine 11 (888 mg, 1.57 mmol) was dissolved under heat in chloroform (83 ml) and after cooling down to 0 °C conc. acetic acid (83 ml) was added. To this solution, NBS (588 mg, 3.3 mmol, 2.1 eq.) was added in one portion and the mixture was stirred in darkness at ambient temperature for one hour. Then the mixture was extracted carefully with a saturated solution of sodium hydrogen carbonate and washed several times with water. The organic phase was dried over sodium sulfate and the solvent was removed under reduced pressure. Column chromatography (silica, DCM : n-hexane = 2 : 1) yielded the desired product 12 (965 mg, 1.34 mmol, 85%) as deep blue powder. M.p.: 198-200 °C. ¹H NMR (CDCl₃, 400 MHz) δ ppm: 7.58–7.53 (m, 4H, Phenyl), 7.40–7.30 (m, 6H, Phenyl), 2.98 (q, ${}^{3}J = 7.6$ Hz, 4H, CH₂), 2.66 (q, ${}^{3}J = 7.6$ Hz, 4H, CH₂), 1.30 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃), 1.19 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃). ${}^{13}C$ NMR (CDCl₃, 100 MHz) δ ppm: 152.79, 142.88, 140.76, 138.89, 137.97, 130.07, 129.03, 128.54, 128.13, 124.39, 112.74, 22.37, 21.77, 14.73, 14.19. MS (MALDI-TOF): 720.0 [M]⁺ (calc. for $C_{34}H_{30}Br_2N_2S_3$: 720.0). Elemental analysis: calc. (%) for C₃₄H₃₀Br₂N₂S₃: C, 56.51; H, 4.18; N, 3.88%; found: C, 56.49; H, 4.21; N, 3.73.

Thien-2-yl-[1,3]dioxolane (13). Thiophene-2-carbaldehyde (15.5 g, 134 mmol), ethylene glycol (12.58 g, 203 mmol) and a catalytic amount of *p*-toluenesulfonic acid (38 mg, 0.20 mmol) were dissolved in toluene (50 ml). The solution was refluxed and stirred for 2 hours at 160 $^{\circ}$ C oil bath temperature and water was continuously removed by a Dean–Stark apparatus. Reaction control was performed by gas chromatography (GC), showing that ethylene glycol was removed in parts with the formed water. Therefore, more glycol was added dropwise, until complete turnover was observed by GC. Then the reaction mixture was washed with aqueous solution of sodium hydrogen carbonate and water. The organic phase was separated, dried over sodium sulfate and the solvent was removed under reduced pressure.

Fractional distillation over Vigreux gave the product (13.1 g, 84 mmol) as colorless liquid in a yield of 63%. B.p.: 108–110 °C (14 mbar). ¹H NMR (CDCl₃, 400 MHz) δ ppm: 7.33 (dd, J = 5.0 and 1.3 Hz, 1H, Th-H), 7.18 (ddd, J = 3.5 Hz, 1.2 Hz and 0.7 Hz, 1H, Th-H), 7.00 (dd, J = 5.0 Hz and 3.5 Hz, 1H, Th-H), 6.11 (s, 1H, OCH), 4.15–4.06 (m, 2H, CH₂), 4.02–3.94 (m, 2H, CH₂). ¹³C NMR (CDCl₃, 100 MHz) δ ppm: 126.6, 126.3, 126.2, 100.3, 67.8, 66.8, 65.2. Analytical data are according to the literature.⁵⁰

2-(5-[1,3]Dioxolan-2-yl-thien-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (14). To a solution of dioxolane 13 (6.0 g, 38.4 mmol) in freshly dried THF (60 ml) was added slowly nBuLi (25.2 ml of a 1.6 M solution in *n*-hexane, 40.3 mmol, 1.05 eq.) at -78 °C and under argon atmosphere. Stirring was continued for 15 minutes at -78 °C. Then the cooling bath was removed and the reaction mixture was stirred for 45 minutes. The mixture was cooled again to -78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (ITDB) (8.62 ml, 42.2 mmol, 1.1 eq.) was added slowly. The cooling bath was removed and stirring was continued for two hours. Finally the mixture was extracted with diethyl ether and aqueous solution of bicarbonate. The organic phase was separated, dried over sodium sulfate and the solvent was removed under reduced pressure. The product (9.46 g, 33.5 mmol) crystallized as a wax like yellow solid in a yield of 87%. The obtained material was pure enough for further syntheses. ¹H NMR (CDCl₃, 400 MHz) δ ppm: 7.51 (d, ${}^{3}J = 3.5$ Hz, 1H, Th-H), 7.20 (dd, J = 3.5 Hz and 0.5 Hz, 1H, Th-H), 6.17 (s, 1H, OCH), 4.15-4.06 (m, 2H, CH₂), 4.06-3.97 (m, 2H, CH₂), 1.33 (s, 12H, CH₃). ¹³C NMR (CDCl₃, 100 MHz) δ ppm: 149.2, 136.8, 127.1, 100.1, 84.1, 65.1, 24.7. MS (EI): m/z = 282 ([M]⁺, 100), 195 (50), 124 (45).

5,7-Bis(5'-(1,3-dioxolan-2-yl)-3,4-diethyl-2,2'-bithien-5-yl)-2,3diphenylthieno[3,4-b]pyrazine (15). Dibromo-terthiophene 12 (600 mg, 0.83 mmol), dioxoborolane 14 (773 mg, 2.74 mmol, 3.3 eq.), HP('Bu)₃BF₄ (77 mg, 0.27 mmol) and Pd₂(dba)₃·CHCl₃ (69 mg, 0.08 mmol) were dissolved in freshly dried THF (50 ml). Aqueous solution of K_3PO_4 (2 mol L⁻¹, 4.25 g in 10 ml of water) was added and the mixture was irradiated by microwave for 40 minutes at 90 °C. TLC (silica, DCM : cyclohexane : triethylamine = 67: 30: 3) showed complete turnover and the mixture was then extracted with water and DCM. The organic phase was dried over Na₂SO₄ and freed from the solvent under reduced pressure. Column chromatography (silica, DCM : cyclohexane : triethylamine = 67:30:3) furnished **15** (58 mg, 0.07 mmol) as green powder (lilac in solution) in a yield of 89%. M.p.: 183-185 °C. ¹H NMR (CD₂Cl₂, 400 MHz) δ ppm: 7.54–7.49 (m, 4H, Phenyl), 7.35–7.25 (m, 6H, Phenyl), 7.10 (dd, ${}^{3}J = 3.7$ Hz and 0.52 Hz, 2H, Th-H), 7.07 (s, 1H, Th-H), 7.06 (s, 1H, Th-H), 6.07 (s, 2H, C-H), 4.12-4.08 (m, 4H, O-CH₂), 3.99-3.95 (m, 4H, O-CH₂), 2.98 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂–CH₃), 2.80 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂-CH₃), 1.27 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃), 1.22 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃). ¹³C NMR (CD₂Cl₂, δ ppm) 152.94, 143.39, 142.42, 141.46, 139.52, 138.62, 137.53, 133.34, 130.36, 129.25, 128.40, 127.91, 127.06, 126.00, 125.32, 100.62, 65.71, 22.17, 21.26, 15.64, 14.96. MS (MALDI-TOF): m/z 872.3 [M]⁺ (calc. for $C_{48}H_{44}N_2O_4S_5$: 872.2). Elemental analysis: calc. (%) for C48H44N2O4S5: C, 66.02; H, 5.08; N, 3.21%; found: C, 66.02; H, 5.19; N, 3.12.

5',5''-(2,3-Diphenylthieno[3,4-b]pyrazine-5,7-diyl)bis(3',4'diethyl-2,2'-bithiophene-5-carbalde-hyde) (16). Dioxolane 15 (88 mg, 0.1 mmol) was dissolved in THF (8 ml). Water (2 ml) and a catalytic amount of p-toluenesulfonic acid (10 mg) were added. The solution was stirred for 12 h at rt. After that, reaction control by TLC (100% DCM) showed complete turnover and the solvent was removed under reduced pressure. The solution was then extracted with DCM and water. The organic phase was dried over Na₂SO₄ and the solvent was removed by rotary evaporation. Bis-aldehyde 16 (43 mg, 0.05 mmol) was isolated by column chromatography on silica (100% DCM) as deep green powder in a yield of 54%. M.p.: 248-250 °C. ¹H NMR (CDCl₃, 400 MHz) δ ppm: 9.91 (s, 2H, OHC), 7.67 (d, ${}^{3}J = 4.0$ Hz, 2H, Th-H), 7.62– 7.57 (m, 4H, Ar-H), 7.42–7.31 (m, 8H, Ar-H), 3.06 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 2.91 (q, ${}^{3}J = 7.5$ Hz, 4H, CH₂), 1.36 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃), 1.30 (t, ${}^{3}J = 7.5$ Hz, 6H, CH₃). ${}^{13}C$ NMR (CDCl₃, 100 MHz) δ ppm: 182.60, 152.87, 146.49, 143.04, 142.90, 142.38, 138.80, 138.43, 136.86, 132.21, 130.10, 129.69, 129.19, 128.18, 126.22, 124.84, 21.89, 21.14, 15.06, 14.63. MS (HR MALDI-TOF): 785.1459 $[M + H]^+$ (calc. for $C_{44}H_{36}N_2O_2S_5$: 784.1453).

2,2'-(5',5''-(2,3-Diphenylthieno[3,4-b]pyrazine-5,7-diyl)bis(3',4'diethyl-2,2'-bithien-5',5-diyl))-bis(methan-1-yl-1-ylidene)dimalononitrile (3). Bis-aldehyde 16 (482 mg, 0.61 mmol) was dissolved in 1,2-dichloroethane (170 ml) and malononitrile (812 mg, 12.3 mmol, 20 eq.) was added at room temperature. Finally piperidine (0.12 ml, 1.23 mmol) was added and the resulting solution was stirred at room temperature for twelve hours, after which reaction control by TLC (100% DCM) showed complete conversion. After extracting the mixture with DCM, the organic phase was washed with water, dried over Na₂SO₄ and freed from the solvent under reduced pressure. To remove most of the side products, column chromatography on silica with first pure DCM and later a mixture of DCM and ethyl acetate (9:1) was applied. A second column chromatography (silica, methanol : ethyl acetate = 1 : 1) was performed to eluate impurities, while the product remained on the column head. The product was then extracted from silica with pure DCM. Removal of the solvent under reduced pressure furnished title compound 3 (31 mg, 0.04 mmol) as dark violet powder in a yield of 66%. M.p.: 336 °C. ¹H NMR (CD₂Cl₄, 500 MHz, 100 °C) δ ppm: 7.73 (d, ${}^{3}J = 4.2$ Hz, 2H, Th-H), 7.70 (s, 2H, Vinyl), 7.60-7.56 (m, 2H, Th-H), 7.39-7.29 (m, 8H, Phenyl), 3.06 (q, ${}^{3}J = 7.6$ Hz, 4H, CH₂), 2.92 (q, ${}^{3}J = 7.6$ Hz, 4H, CH₂), 1.35 (t, ${}^{3}J = 7.4$ Hz, 6H, CH₃), 1.30 (t, ${}^{3}J = 7.4$ Hz, 6H, CH₃). MS (MALDI-TOF): m/z 880.4 [M]⁺ (calc. for C₅₀H₃₆N₆S₅: 880.2). Elemental analysis: calc. (%) for C₅₀H₃₆N₆S₅: C, 68.15; H, 4.12; N, 9.45%; found: C, 68.24; H, 4.22; N, 9.60%.

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