Dye-functionalized head-to-tail coupled oligo(3-hexylthiophenes)— perylene–oligothiophene dyads for photovoltaic applications†

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A series of novel donor–acceptor systems, consisting of head-to-tail coupled oligo(3-hexylthiophene)s covalently linked to perylenemonoimide, is described. These hybrid molecules, which differ by the length of the oligothiophene units from a monothiophene up to an octathiophene, were created via effective palladium-catalyzed Negishi and Suzuki cross-coupling reactions in good to excellent yields. The optical and electrochemical properties of these compounds were determined and based on this series structure–property relationships have been established which give vital information for the fabrication of photovoltaic devices. Because the synthesized perylenyl–oligothiophenes distinguish themselves by a high absorption between 300 and 550 nm and an almost complete fluorescence quenching of the perylene acceptor, they meet the requirements for organic solar cells.

Introduction

Head-to-tail coupled poly(3-alkylthiophenes) (P3AT) are intensively investigated (semi)conducting polymers due to well established synthetic procedures and due to their outstanding electronic and charge transport properties.[1] In particular, the understanding and control of their self-organizing properties has led to materials with excellent charge carrier mobilities[2] which allow their application in organic electronic devices. Spin-coated composite films of P3ATs as electron donor and fullerene derivatives as electron acceptor have been used successfully as the active layer in plastic photovoltaic devices leading to conversion efficiencies of around 3.5% which are among the highest values for plastic solar cells.[3]

The synthesis and investigation of structurally defined conjugated oligomers,[4] in particular oligothiophenes,[5] as models for the corresponding polymers and as materials in their own right has led to valuable structure–property relationships and applications in, e.g., organic field effect transistors and circuits,[6] light emitting diodes[7] or in solar cells based on small molecules.[8] In this respect and as models for P3ATs, we recently reported the effective solution- and solid-phase synthesis of a series of monodisperse head-to-tail coupled oligo(3-alkylthiophenes) (HT-O3AT) up to a dodecamer by transition metal-catalyzed cross-coupling reactions of the Suzuki type.[9] The investigation of the physical properties resulted in the typical dependence of the optoelectronic properties on the inverse of the oligomer length.[9a,10] Furthermore, as the polymers, the model oligomers form well-organized self-assembled 2D-crystalline monolayers

at the solid–liquid interface which have been characterized by scanning tunnelling microscopy (STM)[11] and exhibit very promising charge carrier mobilities in thin film field-effect transistors.[12]

In recent years, extensive studies on covalently linked π-conjugated oligomer–acceptor dyad and triad molecules have been performed in order to better understand the photophysics in photovoltaic applications. Combinations of oligothiophenes and C_{60},[13] oligophenylenevinylenes and C_{60}[14] or oligophenylenevinylenes and perylenes[15] were synthesized and their electronic properties as well as electron transfer processes investigated. Perylenes are widely used as chromophores, dyes and pigments since they show outstanding photophysical properties including high absorptivities and fluorescence quantum yields and at the same time are chemically and thermally extremely stable.[16]

Perylenes have been implemented successfully as small molecules in heterojunction solar cells acting as electron transport material and represent an alternative to fullerenes which are frequently used as electron acceptors.[17]

We report here the synthesis of a series of perylene-functionalized head-to-tail coupled O3ATs (**7–9,12,14,16**). The optical and electrochemical properties were investigated in terms of their dependence on the oligothiophene chain length which varies from one to eight thiophene units. The novel type of π-donor π-acceptor dyad molecules was designed in a way that the oligothiophene part should preserve the typical charge transport and self-assembling properties in the solid state, whereas the perylene unit, [N-(2,6-diisopropylphenyl)]-perylene-3,4-dicarboximide, should provide high absorptivity in the visible region as well as electron accepting properties. With respect to the range of absorption, to the energy levels of

† Dedicated to Professor Dr Dr h.c. Franz Effenberger (University of Stuttgart) on the occasion of his 75th birthday.

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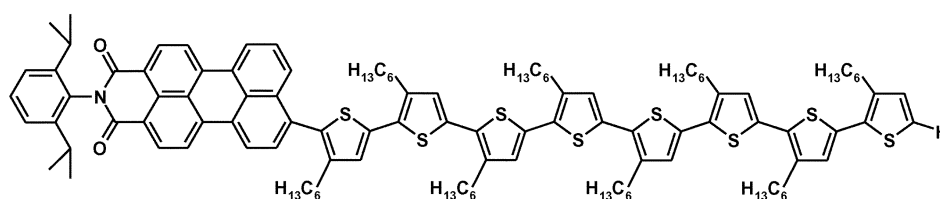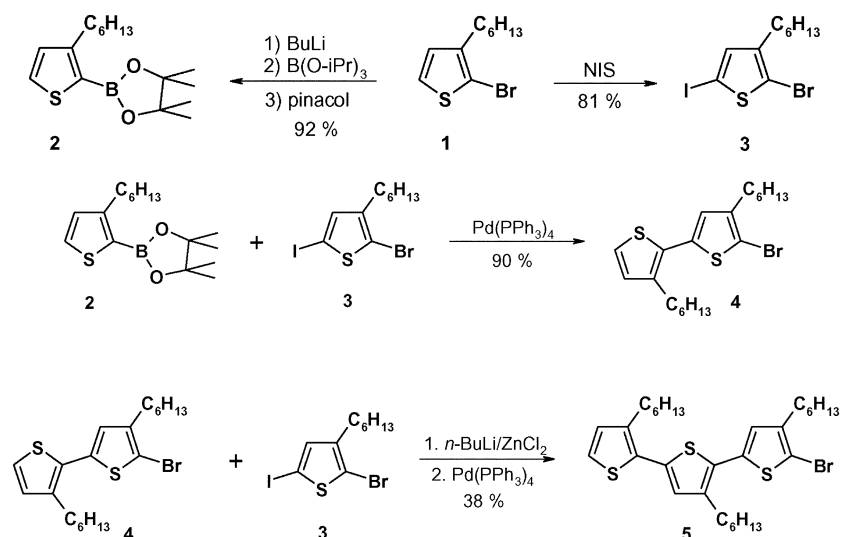
the frontier orbitals and bands in the solid state, respectively, tailored materials for applications in photovoltaic devices are expected from our novel hybrid molecules.

Results and discussion

Synthesis

The straightforward preparation of HT-O3ATs typically demands a substituent at one α-position. For example, a benzyl ester group in the case of a liquid phase[9a] or a Merrifield resin in a solid phase synthesis[9b] at the same time serve as an anchoring and a removable protecting group providing controlled chain growth at only one end of the oligothiophene. A similar strategy was successfully used for the synthesis of the novel donor–acceptor oligomers 7–9,12,14 and 16. The electron-accepting perylene dye acts as the anchor at which the electron-donating oligothiophene chain is stepwise elongated in a modular iterative approach by Pd-catalyzed C–C cross coupling reactions. Starting from 2-bromo-3-hexylthiophene 1,[18] by lithiation with n-butyl lithium (n-BuLi) and reaction with tri(isopropyl)borate and pinacol the corresponding 3-hexylthiophene-2-boronic ester 2 has been synthesized in 92% yield. Selective halogenation of 1 with N-iodosuccinimide (NIS) on the other hand leads to 2-bromo-3-hexyl-5-iodothiophene 3[19] in 81% yield comprising two differently reactive halogen functions.

Suzuki-type cross coupling of both components 2 and 3 yields dihexyl-bithiophene 4[9b] in 90% as a central building block. Following this synthetic strategy the overall yield of 4 could be doubled with respect to a previous published synthesis.[9b] Bithiophene 4 was converted to the corresponding zincate via lithiation

with n-BuLi and metal–metal exchange by zinc chloride. Then, in a Negishi-type reaction under palladium catalysis it was selectively cross-coupled with iodobromothiophene 3 to give the next higher homologue, head-to-tail coupled and isomerically pure trihexyl-terthiophene 5 in 38% yield.

The smaller members of the homologous series of the perylenyl oligothiophenes 7–9 were first synthesized by Negishi coupling of brominated perylene-dicarboximide 6 and the zincates of α-bromothiophenes 1,4 and 5. Reaction of monothiophene 1 led to perylenyl thiophene 7 in 62% yield, of bithiophene 4 to corresponding dye-functionalized bithiophene 8 in 76% yield and of terthiophene 5 to the trimeric member of the series, perylenyl-terthiophene 9 in 35% yield.

Because zincates of longer oligothiophenes are less stable, this synthesis was rather less promising for the efficient preparation of longer homologues. Therefore, we used a method recently developed by us for the step-wise build-up of longer HT-O3ATs in the solid phase.[9b] With the adaptation of this strategy, perylenyl-oligothiophenes 8 (n = 2), 12 (n = 4), 14 (n = 6) and 16 (n = 8) became accessible in excellent yields. From bromobithiophene 4 the corresponding boronic acid pinacol ester 10 was synthesized in 98% yield representing the crucial module which then will be added to the growing oligothiophene chain. Subsequent palladium-catalyzed Suzuki cross-coupling of boronic ester 10 with 9-bromoperylene dicarboximide 6 gave perylenyl bithiohene 8 in higher yield (90%) than obtained before for the reaction of the corresponding zincate.

For the iterative step-wise elongation of the oligothiophene chain selective iodination at the reactive α-position of the bithiophene moiety was achieved by a mercuration/iodination sequence[9b] yielding iodinated derivative 11 in 97% yield. Subsequent Suzuki coupling with boronic ester 10 very efficiently gave
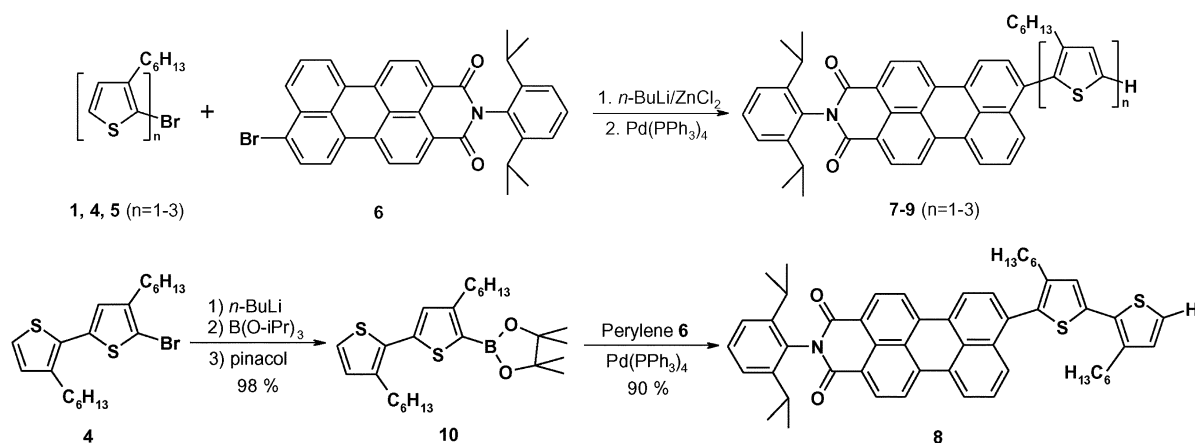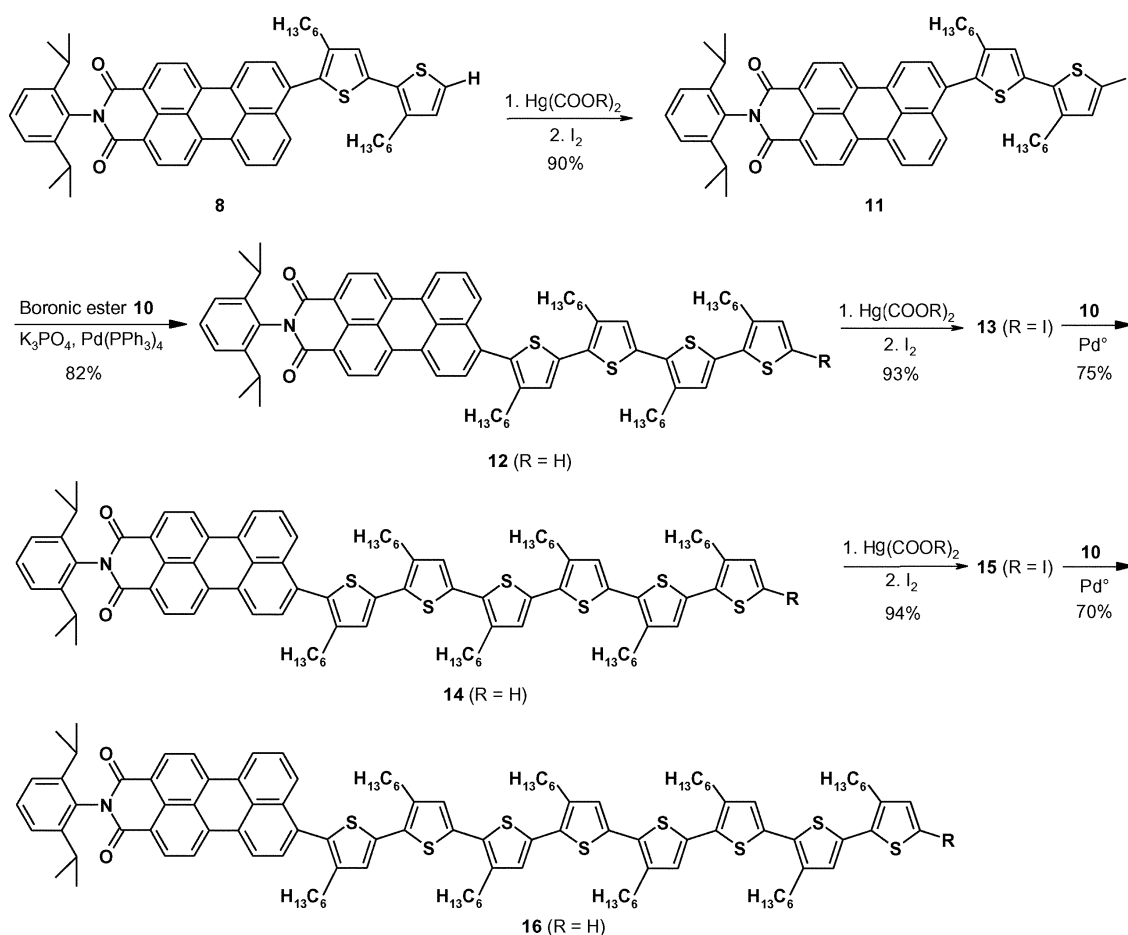
the next homologue, perylenyl-quaterthiophene **12**, in 82% yield. We continued this iodination/cross-coupling protocol to produce iodinated perylenyl-quaterthiophene **13** in 93%, perylenyl-sexithiophene **14** in 75%, iodinated perylenyl-sexithiophene **15** in 94% and finally perylenyl-octathiophene **16** as the longest representative in the series in 70% yield. With this, a whole series of dye-functionalized HT-O3ATs, including one to eight thiophene units were effectively synthesized.

Electronic properties

In homologous series of oligomers, their properties can be investigated as a function of chain length. Therefore, clear structure–property relationships become observable. For conjugated oligomeric systems it has been shown experimentally and theoretically that typically the (electronic) properties linearly depend on the inverse of the conjugated chain length.[11] For the series of dye-functionalized HT-O3ATs **7–9,12,14** and **16** optical and redox properties were determined and an energy level diagram of the frontier orbitals was deduced from the data set. The absorption and emission maxima, fluorescence quantum yields and the optical energy gaps for the complete series are given in Table 1 and compared to the individually synthesized parent building blocks. The energy gaps were determined from the onset of the longest wavelength absorption band of the hybrid molecules.

Absorption and emission spectra were measured in chloroform ($c = 5 \times 10^{-5}$ mol l^{-1}) (Fig. 1) and in the solid state as spin-coated thin films (Fig. 2). N-(2,6-Diisopropylphenyl)perylene-3,4-dicarboximide (**PDCI**) was taken as a reference which shows three absorption bands: the most intense is located at $\lambda_1 = 265$ nm, a structured very weak band at $\lambda_2 = 355$ nm (not included in Table 1) and the well structured, very intense π–π* transition band at $\lambda_3 = 486$ nm with a shoulder at 509 nm which reflects a rather planar aromatic system. The coupling of thiophene units to the parent perylene system in compounds
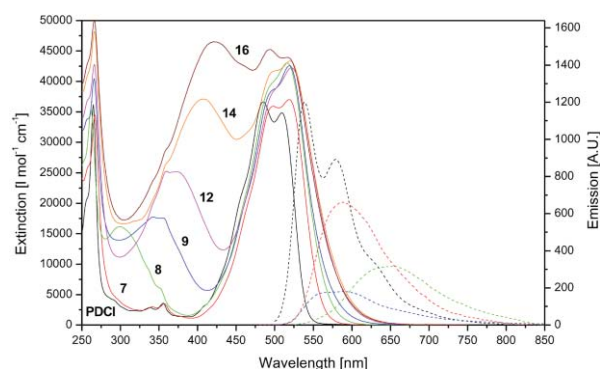
Fig. 1 UV-Vis spectra of the perylenyl-oligothiophenes **7–9,12,14** and **16** and reference compound **PDCI** in chloroform ($c = 5 \times 10^{-5}$ mol l^{-1}) (full lines). Emission spectra of **PDCI** and compounds **7–9** are added (dashed lines). The other compounds are omitted for clarity.

7–9,12,14 and **16** induces a change in the vibronic distribution of the π–π* band. With growing oligothiophene chain length a red-shift of this band ($\Delta\lambda = 14$–22 nm) can be determined by using the parameter "full width at half maximum" (FWHM).[21] Consequently, an increased tendency to a tailing of the curve on the low energy side of the π–π* band is clearly visible. A detailed analysis has been made by calculating the difference absorption spectra of all perylenyl-oligothiophenes **7–9,12,14–16** and reference compound **PDCI**. As a result a new weak absorption band in the regime of 534–538 nm irrespective of the oligothiophene chain length appears. We attribute this band to a charge-transfer (CT) transition according to the fluorescence results discussed below.[22]

In the absorption spectra, starting with perylenyl-bithiophene **8** at 300 nm a third band due to the π–π* transition of the oligothiophene moiety arises. With increasing chain length of the oligothiophene, this band gradually becomes more intense

Table 1 Optical properties of the perylenyl-oligothiophenes **7–9,12,14,16** in solution and in the solid state in comparison to **PDCI**. P denotes perylene, OT oligothiophene

Chromophor	Solution								Solid state		
	λ^{abs}_1 (P)/nm	lg ε	λ^{abs}_2 (OT)/nm	lg ε	λ^{abs}_3 (P)/nm[a]	$\Delta E_{opt.}$/eV	λ^{em}/nm[a]	ϕ^{em} (%)[b]	λ^{abs}_2 (OT)/nm	λ^{abs}_3 (P)/nm[a]	$\Delta E_{opt.}$/eV
PDCI	265	4.56			486, 509	2.30	539, 579	90		501, 523	2.11
7 (1T)	267	4.54			497, 519	2.22	588	67		505, 529	2.10
8 (2T)	261	4.55	300 (302)[c]	4.21	497, 517	2.19	655 (367)[c]	37 (2)[c]		502, 526	2.09
9 (3T)	266	4.61	357	4.24	498, 520	2.18	563	21	361	503, 530	2.09
12 (4T)	266	4.63	375 (371)[d]	4.40	500, 522	2.13	595 (494)[d]	1 (13)[d]	386	503, 530	2.03
14 (6T)	266	4.68	408 (406)[e]	4.55	500, 520	2.12	590 (534)[e]	1 (29)[e]	437	495, 527	2.02
16 (8T)	266	4.70	422 (422)[f]	4.64	494, 518	2.12	600 (560)[f]	1 (31)[f]	464	490, 524	2.02

[a] Maxima in italics. [b] Excitation wavelength $\lambda^{ex} = 480$ nm. [c] For comparison values of the parent non-functionalized dihexyl-bithiophene, [d] tetrahexyl-quaterthiophene, [e] hexahexyl-sexithiophene, [f] octahexyl-octathiophene[20] are given in parentheses.
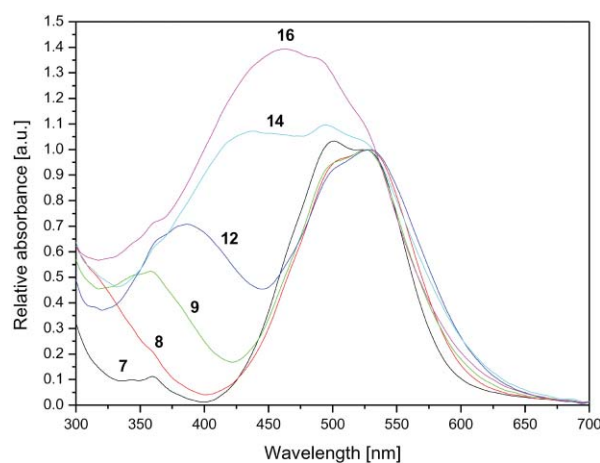
Fig. 2 Solid-state UV-Vis spectra of thin films of the perylenyl-oligothiophenes **7–9,12,14** and **16** spin-coated on glass (normalized to the maximum of the perylene absorption band).

and red-shifted finally reaching $\lambda_2 = 422$ nm for the perylenyl-octithiophene **16**. The position of this band compares well to the absorption maxima of the parent non-functionalized HT-O3HTs[20] indicating that the two chromophoric subunits in the dyads are rather electronically decoupled due to steric interactions of the perylene system with the adjacent 3-hexylthiophene unit. In the same line, the optical band gap is gradually diminished on going from **PDCI** ($\Delta E = 2.30$ eV) to perylenyl-quaterthiophene **12** ($\Delta E = 2.13$ eV) and then remains constant with increasing oligothiophene length.

Corrected emission spectra for the whole series of compounds were measured in chloroform (Table 1, Fig. 1). While the emission band of the reference compound **PDCI** ($\lambda_{max} = 539$ nm) is very intense (fluorescence quantum yield of $\phi = 90\%$[23]) and shows a vibronic splitting, the hybrid compounds exhibit less structured and broader emission bands whose maxima with respect to **PDCI** are significantly shifted to the red. With increasing oligothiophene length, the intensity of the emission bands and the quantum yields progressively decrease to 67% for perylenyl-monothiophene **7**, to 37% for bithiophene **8**, to 21% for terthiophene **9** and to values around 1% for the longer homologues **12,14** and **16** when excited at 480 nm. Excitation at wavelengths corresponding to the oligothiophene absorption (300–400 nm) results in a weak fluorescence in the regime of the perylene emission, whereas this from the oligothiophene part is completely quenched. As a reference, the pure non-functionalized HT-O3ATs show a structured emission whose intensity increases with the enlargement of the conjugated backbone.[23] For the smaller homologues of this series, **7** and **8**, the emission band is strongly red-shifted ($\lambda^{em}_{FWHM} = 602$ and 656 nm) with respect to **PDCI** ($\lambda^{em}_{FWHM} = 562$ nm).[24] This trend is reversed for the longer homologues finally leading to $\lambda^{em}_{FWHM} = 596$ nm in the case of octathiophene **16**. Perylenyl-oligothiophenes **7–9** were subjected to a more detailed study concerning the influence of the solvent polarity on the emission properties. For compounds **7** and **8** we find a positive solvatochromism which is a clear indication that the observed emission band has a CT character. However, for perylenyl-terthiophene **9** we observe a much more complicated behaviour suggesting other competitive relaxation processes.[24] These results are in accordance with an expected photo-induced electron transfer from the oligothiophene donor to the perylene acceptor which already has been investigated for derivatives **7** and **8**.[25]

Thin films of the hybrid molecules **7–9,12,14** and **16** (thicknesses 34–50 nm) were obtained by spin-coating of corresponding toluene solutions ($c = 20$ mg ml^{-1}) onto a glass substrate (Fig. 2). Absorption spectra in the solid state show the same trends and compared to the solution spectra in

general a broadening and red-shift of the bands are visible and consequently lead to smaller band gaps ($\Delta\Delta E_{opt} \approx 0.10$ eV). The displacement is small for the absorption band of the perylene moiety ($\Delta\lambda_3 = 4$–12 nm), but rather pronounced for the oligothiophene chains and steadily increasing with increasing chain length ($\Delta\lambda_2 = 4$–42 nm). With respect to applications in solar cells, in particular the absorption behaviour of the longer members **14** and **16** in the series cover a broad range of the visible spectrum (300–700 nm) with high optical densities.

Electrochemical properties

Optical measurements provide an estimation of the energy difference of the frontier orbitals and therefore of the (optical) band gap ΔE_{opt}. However, with respect to solar cell applications it is in particular of great importance to ascertain the absolute energetic positions of the HOMOs and LUMOs which can be derived from redox potentials. Oxidation and reduction potentials of the perylenyl-oligothiophenes **7–9,12,14** and **16** were determined by cyclic voltammetry (CV) in dichloromethane ($c = 1 \times 10^{-3}$ mol l^{-1}) using tetrabutylammonium hexafluorophosphate (TBAHFP) as the supporting salt (Fig. 3). Reduction and oxidation potentials are given *versus* the internal standard ferrocene–ferricenium (Fc/Fc$^+$) and are compared to the reference compound **PDCI** and the parent non-functionalized HT-O3ATs which facilitates the assignment of the individual redox waves. The potential difference between the onset of the first oxidation and the first reduction wave gives the electrochemically determined band gap ΔE_{CV} which can be compared to the optical band gap ΔE_{opt} (Table 2). The peryleneimide **PDCI**
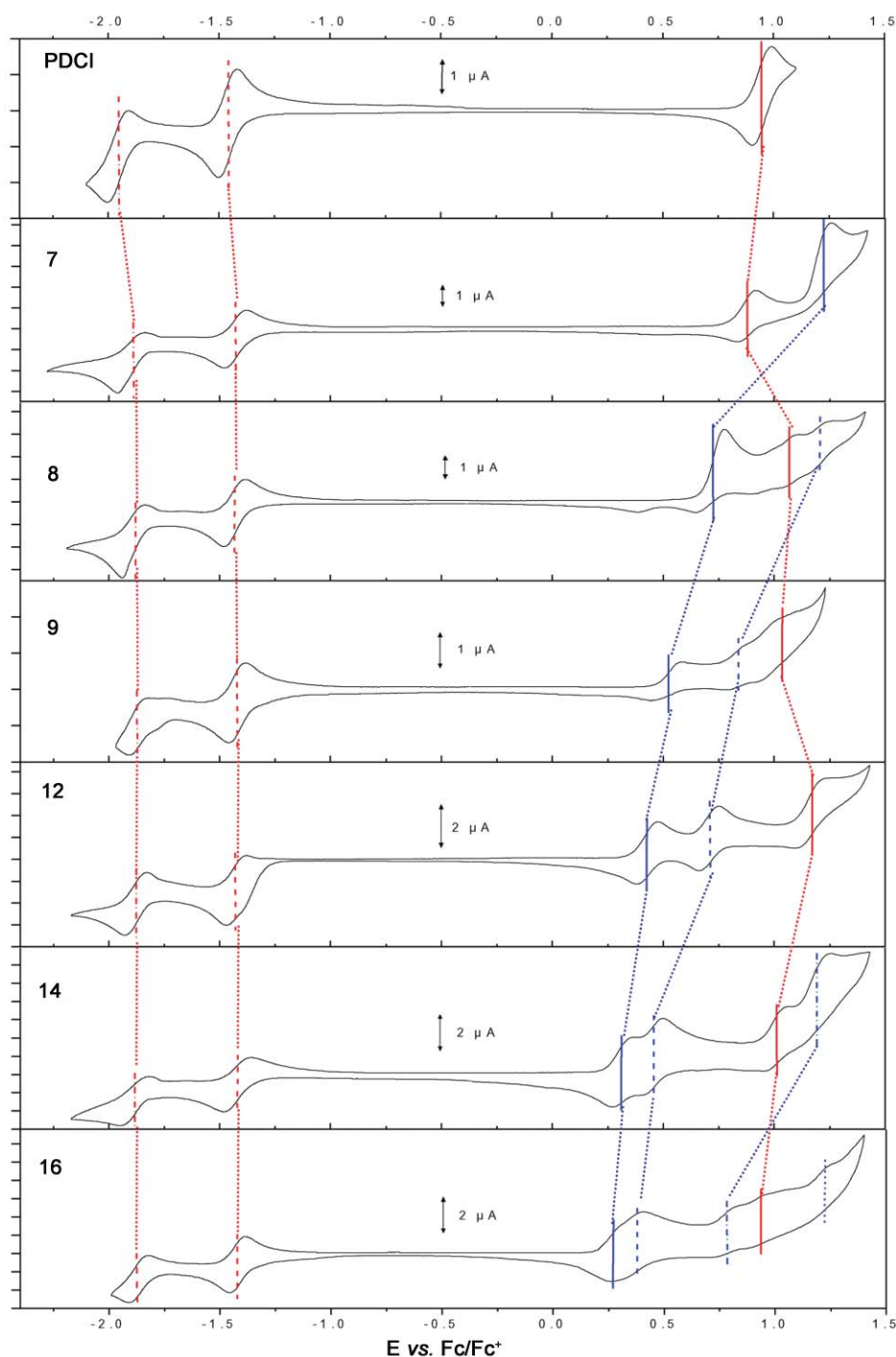
Fig. 3 Electrochemical characterization of the perylenyl-oligothiophenes **7–9,12,14** and **16** in dichloromethane–TBAHFP (0.1 M), scan speed 100 mV s^{-1}, potentials *vs.* Fc/Fc$^+$. Red bars correspond to redox processes of the perylene unit, blue bars to those of the oligothiophene unit.

Table 2 Electrochemical properties of the perylenyl-oligothiophenes **7–9,12,14,16** and **PDCI**, $c = 1 \times 10^{-3}$ mol l^{-1}, in dichloromethane–TBAHFP (0.1 M) *vs.* Fc/Fc$^+$ at 100 mV s^{-1} (P denotes perylene, OT oligothiophene)

Compound	E°_{red2} (P)/V	E°_{red1} (P)/V	E°_{ox1} (P)/V	E°_{ox1} (OT)/V	E°_{ox2} (OT)/V	E°_{ox3} (OT)/V	E°_{ox4} (OT)/V	$\Delta E_{CV}{}^a$/eV
PDCI	−1.95	−1.46	0.95					2.24
7 (1T)	−1.88	−1.43	0.88	1.21[b]				2.14
8 (2T)	−1.87	−1.42	1.06	0.71[b] (*0.83*)[c]	1.20[b] (*1.24*)[c]			2.02
9 (3T)	−1.87	−1.42	1.04	0.52	0.84			1.80
12 (4T)	−1.87	−1.42	1.17	0.43 (*0.43*)[d]	0.71 (*0.85*)[d]			1.63
14 (6T)	−1.88	−1.42	1.01	0.31 (*0.30*)[e]	0.45 (*0.43*)[e]	1.19[b] (*1.20*)[e]		1.58
16 (8T)	−1.87	−1.42	0.93	0.27 (*0.25*)[f]	0.38 (*0.34*)[f]	0.78 (*0.79*)[f]	1.19[b] (*1.21*)[f]	1.54

[a] Determined by $\Delta E_{CV} = E'_{ox1} - E'_{red1}$ (E' is the onset potential at which the redox process starts). [b] Irreversible redox process, E° determined at $I^\circ = 0.855 \times I_p$.[26] [c] Redox potentials for the parent non-functionalized dihexyl-bithiophene, [d] tetrahexyl-quaterthiophene, [e] hexahexyl-sexithiophene, [f] octahexyl-octathiophene.[20]

exhibits two reversible reduction waves ($E^\circ_{red1(P)} = -1.46$ V, $E^\circ_{red2(P)} = -1.95$ V) and one reversible oxidation wave ($E^\circ_{ox1(P)} = 0.95$ V), indicating the formation of stable radical anions, dianions, and radical cations, respectively. As a general trend, for the perylenyl-oligothiophenes **7–9,12,14** and **16** both reduction processes are slightly facilitated and shifted positively by only $\Delta E^\circ \leq 80$ mV, but are independent of the oligothiophene chain length. The successive coupling of 3-hexylthiophene units to the parent perylene system leads to more complex CVs in the positive potential regime. This is due to the interference of the perylene with the oligothiophene oxidation processes. The detailed analysis of the various redox transitions in comparison to the CVs of the non-functionalized HT-O3ATs which allow us an assignment of the individual redox waves, clearly reveals that a complicated mutual influence of the two electrophoric subunits exists.

In the case of the 1T-derivative **7** the first redox wave at $E^\circ_{ox1(P)} = 0.88$ V corresponds to the oxidation of the perylenyl moiety to the radical cation. In comparison to the parent compound **PDCI** this value is slightly shifted to the negative ($\Delta E^\circ = 70$ mV) because the monothiophene unit which is (irreversibly) oxidized at quite higher potential ($E^\circ_{ox1(OT)} = 1.21$ V) is therefore neutral and increases the overall conjugation. This conclusion is further supported by the fact that also the oxidation of the monothiophene unit is facilitated and shifted to negative potentials compared to pristine 3-hexylthiophene (for comparison $E^\circ_{ox1} = 1.56$ V for 3-methylthiophene).[27] With increasing chain length of the oligothiophene, the first oxidation potential of this unit is gradually shifted to the negative (to $E^\circ_{ox1(OT)} = 0.27$ V for octamer **16**) and successively an increased number of redox processes occur (up to four for **16**). This is a well known behaviour in homologous series of conjugated oligomers[28] and has been analyzed in detail for the series of the non-functionalized HT-O3ATs.[9a] In contrast to 1T-derivative **7**, in perylenyl-2T **8** the oxidation of the bithiophene unit occurs at a lower potential ($E^\circ_{ox1(OT)} = 0.71$ V) than that of the perylene unit ($E^\circ_{ox1(P)} = 1.06$ V) which in turn is shifted to the positive ($\Delta E^\circ = 0.18$ V) because the oligothiophene unit is now positively charged (radical cation) and withdraws electron density from the perylene system. In the case of homologue **9**, the first oxidation process ($E^\circ_{ox1(OT)} = 0.52$ V) is clearly attributed to the formation of a terthiophene radical cation. However, the assignment of the second and third oxidation waves which lie quite close could only be performed with the help of a correlation of the redox potentials with the inverse chain length ($1/n$) (Fig. 4). The $1/n$ plot shows us that the oxidation wave at $E^\circ_{ox2(OT)} = 0.84$ V should correspond to the formation of a terthiophene dication whereas that at $E^\circ_{ox1(P)} = 1.04$ V belongs to the oxidation of the perylenyl moiety. For perylenyl-4T **12** the situation is unambiguous and we see two well-pronounced reversible redox waves for the oxidation of the oligothiophene ($E^\circ_{ox1(OT)} = 0.43$ V, $E^\circ_{ox2(OT)} = 0.71$ V) to the radical cation and the dication, respectively. Consequently, the oxidation of the perylenyl unit is shifted to the positive ($E^\circ_{ox1(P)} = 1.17$ V). For
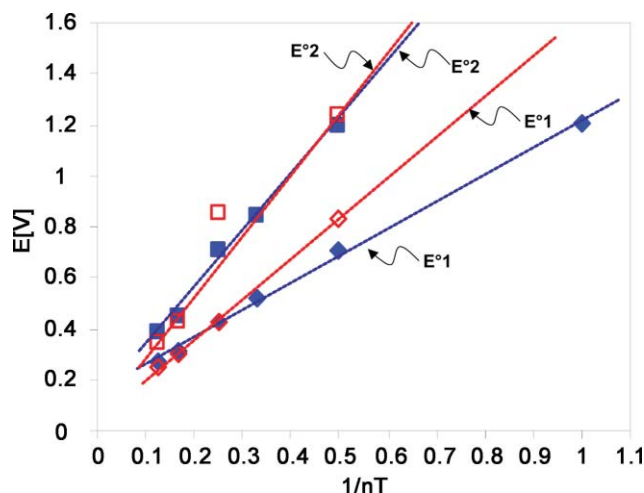
Fig. 4 Correlation of redox potentials (E°_{ox1} and E°_{ox2}) *versus* reciprocal chain length of the oligothiophene unit ($1/n$T) of the perylenyl-oligothiophenes **7–9,12,14** and **16** (blue squares) in comparison to the corresponding non-functionalized oligo(3-alkylthiophenes) (red squares).

the hexamer **14**, the same situation is observed whereby due to the more extended π-system all three potentials lie negative in comparison to those of the tetramer **12**. The oxidation of the oligothiophene chain to the radical trication is observable at $E^\circ_{ox3(OT)} = 1.19$ V. Finally, in perylenyl-octathiophene **16**, the four waves are again shifted to the negative and an additional redox process at $E^\circ_{ox4(OT)} = 1.19$ V arises due to the formation of oligothienyl tetracations.

A useful approach to elucidate structure–property relationships in oligomer series is the correlation of physical properties with the inverse of the conjugated chain length. Typically a linear behaviour is found for chain lengths up to 9–11 repeating units, whereas for longer chains, a beginning saturation of the effective conjugation is identified.[9a,10a] In this respect, we correlated the first and second oxidation potential of the oligothiophene units in the hybrid systems **7–9,12,14** and **16** with the inverse of the chain length of the corresponding oligothiophene unit ($1/n$T) (Fig. 4). A linear behaviour is obtained for both oxidation processes (blue squares) whereby the straight lines approach each other for increasing chain lengths. The slopes of the regression lines are less steep compared to those of the parent O3ATs (red squares) indicating that in the hybrid systems the subunits are not fully decoupled and the perylene is slightly contributing to the overall conjugation. As expected, this influence becomes less pronounced for longer oligothiophene chains.

The band gaps ΔE_{CV} were determined from the CVs by taking the difference between the onset of the first oxidation and reduction process (Table 2). The band gap gradually becomes smaller when going from reference compound **PDCI** (2.24 eV)

Table 3 Absolute MO energies of the perylenyl-oligothiophenes 7–9,12,14,16 in comparison to **PDCI** with respect to the vacuum level (P denotes perylene, OT oligothiophene)

Compound	LUMO − 1/eV	LUMO/eV	HOMO/eV	HOMO − 1/eV	HOMO − 2/eV	HOMO − 3/eV	HOMO − 4/eV	$E_g{}^a$/eV
PDCI	−2.85 (P)	−3.34 (P)	−5.75 (P)					2.41
7 (1T)	−2.92 (P)	−3.37 (P)	−5.68 (P)	−6.01 (OT)				2.31
8 (2T)	−2.93 (P)	−3.38 (P)	−5.51 (OT)	−5.86 (P)	−6.01 (OT)			2.14
9 (3T)	−2.93 (P)	−3.38 (P)	−5.32 (OT)	−5.64 (OT)	−5.84 (P)			1.93
12 (4T)	−2.93 (P)	−3.38 (P)	−5.23 (OT)	−5.51 (OT)	−5.97 (P)			1.85
14 (6T)	−2.92 (P)	−3.38 (P)	−5.11 (OT)	−5.25 (OT)	−5.81 (P)	−5.99 (OT)		1.73
16 (8T)	−2.93 (P)	−3.38 (P)	−5.07 (OT)	−5.18 (OT)	−5.58 (OT)	−5.73 (P)	−5.99 (OT)	1.68

^{a} Determined by $E_g = E_{LUMO} − E_{HOMO}$.

to perylenyl-octathiophene **16** (1.54 eV) reflecting the decreasing oxidation potential of the oligothiophene subunit. If one compares ΔE_{CV} with the optically determined band gap ΔE_{opt} only the values for **PDCI** and the perylenyl monothiophene **7** are in good agreement, whereas for the higher homologues ΔE_{CV} is substantially smaller. While the reduction is always due to the perylene moiety, the oxidation only corresponds to the perylene unit for **PDCI** and **7** whereas for the longer homologues it is correlated with the oligothiophene units. In contrast, the optical determined band gap is always representing the electronic properties of the perylene unit for all compounds in the series. Therefore, it can be concluded that these donor–acceptor systems consist of almost perfectly separated subunits with only marginal conjugation between the oligothiophene and the perylene moieties.

MO energies

MO energy diagrams are very helpful for the construction and understanding of organic devices in which the fundamental processes are decisively determined by charged states and their corresponding energy level in the active, organic layer.[29] In order to calculate the absolute energies of the HOMO and LUMO levels of **PDCI** and the perylenyl-oligothiophenes **7–9,12,14** and **16** with respect to the vacuum level, the redox data are standardized to the ferrocene–ferricenium couple which has a calculated absolute energy of −4.8 eV.[30] The band gap energies E_g then result from the energy difference between the HOMO and the LUMO levels. The MO energy levels as well as the band gap energies are listed in Table 3 and a corresponding energy level diagram is depicted in Fig. 5. Very clearly it can be seen in the energy diagram that the HOMO–LUMO band gap decreases with increasing chain length of the oligothiophene unit which is mainly due to the constant lowering of the HOMO energy level whereas the LUMO level remains rather constant.
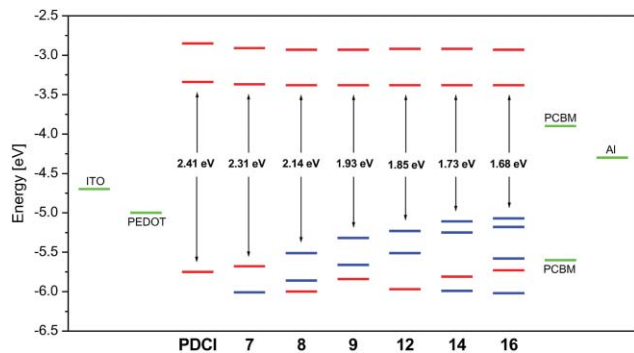
Fig. 5 MO energy level diagram scheme for the perylenyl-oligothiophenes **7–9,12,14** and **16** and reference compound **PDCI**.

The work function of a PEDOT-covered ITO electrode lies higher in energy than the HOMOs of the donor–acceptor systems, allowing holes to be easily injected from the ITO cathode into the photoactive layer. On the other side, the LUMOs of the hybrid systems are energetically higher than both the LUMO of fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) and the work function of aluminium, making them suitable for the manufacturing of photovoltaic devices. First experiments confirm a possible application of this novel type of hybrid materials in organic solar cells. In a standardized setup, bulk-heterojunction devices were manufactured consisting of a PEDOT:PSS-covered ITO cathode, a 1 : 4 mixture of perylenyl-quaterthiophene **12** or octathiophene **16** and PCBM as photoactive layer and a LiF-covered Al anode. These devices exhibited good photoresponses at high open-circuit voltages V_{OC} of 0.94 V and reasonable power conversion efficiencies, which have been calculated for standard test conditions (AM 1.5G, 1000 W m$^{−2}$) (**12**: $\eta = 0.33\%$; **16**: $\eta = 0.48\%$).[31]

Conclusion

We synthesized a series of perylene-functionalized head-to-tail coupled oligo(3-hexylthiophenes) **7–9,12,14** and **16**. The novel donor–acceptor hybrid systems consist of an oligothiophene in which the chain length is systematically varied up to an octamer (donor) and a covalently linked perylene-3,4-dicarboximide (acceptor) and were obtained by palladium-catalysed cross-coupling reactions in excellent yields. Detailed investigations of the electronic properties of the series in solution and in the solid state clearly revealed that there is a systematic change in the spectral range of absorption and emission, the fluorescence quantum yield in solution, redox potentials and energy gaps. Clear structure–property relationships of the novel type of π-donor π-acceptor dyad molecules provide a valuable data set for their application in organic solar cells. The fabrication and characterization of the corresponding photovoltaic devices based on blends of selected perylenyl-oligothiophenes with fullerenes revealed energy conversion efficiencies up to 0.5% under a simulated terrestrial sun spectrum.

Experimental

General procedures

^{1}H-NMR spectra were recorded in CDCl$_3$ on a Bruker AMX 400 at 400 MHz. ^{13}C-NMR spectra were recorded in CDCl$_3$ on a Bruker AMX 400 at 100 MHz. Chemical shifts are denoted in δ units (ppm), and were referenced to internal tetramethylsilane (0.0 ppm). The splitting patterns are designated as follows: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet) and the assignments are *Pery* (perylene), *Ph*, (phenyl), *Th* (thiophene) for ^{1}H-NMR. Mass spectra were recorded with a Varian Saturn 2000 GC-MS and with a MALDI-TOF MS Bruker Reflex 2 (dithranol as the matrix). Elemental analyses were performed on a Perkin-Elmer EA 2400. Melting points were determined with a Büchi B-545 melting point apparatus and are not corrected. Gas chromatography was carried out using a Varian CP-3800 gas chromatograph. HPCL analyses were performed on a Shimadsu SCL-10A equipped with a SPD-M10A photodiode array detector and a SC-10A

solvent delivery system using a LiChrosphor column (Silica 60, 5 µm, Merck). Thin-layer chromatography was carried out on Silica Gel 60 F$_{254}$ aluminium plates (Merck). Developed plates were dried and examined under a UV lamp. Preparative column chromatography was carried out on glass columns of different sizes packed with silica gel Merck 60 (40–63 µm). UV/Vis spectra were taken on a Perkin-Elmer Lambda 19 in 1 cm cuvettes. Thin uniform films for solid-state spectra were obtained on a POLOS wafer spinner from a toluene solution (20 mg ml^{-1}) at 5000 rpm onto a glass substrate. Fluorescence spectra were measured with a Perkin-Elmer LS 55 in 1 cm cuvettes. Fluorescence quantum yields were determined with respect to N-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide (PDCI) ($\Phi = 0.9$ in chloroform[23]) at an excitation wavelength of 480 nm. Cyclic voltammetry experiments were performed with a computer-controlled EG & G PAR 273 potentiostat in a three-electrode single-compartment cell (5 ml). The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of $A = 0.785$ mm^2, which was polished down to 0.5 µm with Buehler polishing paste prior to use in order to obtain reproducible surfaces. The counter electrode consisted of a platinum wire and the reference electrode was an Ag/AgCl secondary electrode. All potential were internally referenced to the ferrocene–ferricenium couple.[30] For the measurements concentrations of 10^{-3} mol l^{-1} of the electroactive species were used in freshly distilled and deaerated dichloromethane (Lichrosolv, Merck) and 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP, Fluka) which was twice recrystallized from ethanol and dried under vacuum prior to use. Solvents and reagents were purified and dried by usual methods prior to use and typically used under inert gas atmosphere. The following starting materials were purchased and used without further purification: n-butyllithium (n-BuLi, Merck) was a 1.6 M solution in n-hexane, N-iodosuccinimide (NIS, ABCR), pinacol (Aldrich), tri(isopropyl)borate (Merck), zinc chloride (Merck), iodine (Merck), 9-bromo-N-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide **6** (BASF). 2-Bromo-3-hexylthiophene[18] **1** and tetrakis(triphenylphosphino)palladium(0)[32] [Pd(PPh$_3$)$_4$] were prepared according to literature procedures.

Synthesis

2-Bromo-3-hexyl-5-iodothiophene (3). 2-Bromo-3-hexylthiophene **1** (22.25 g, 90 mmol) was dissolved in acetic acid (10 ml). After addition of NIS (20.25 g, 90 mmol) the resulting suspension was stirred vigorously for 4 h at 100 °C under light protection. Then the reaction mixture was poured into water (50 ml) and the organic layer was taken off while the water phase was extracted with dichloromethane. The combined organic phases were washed with 1 M sodium hydroxide solution (20 ml), water (20 ml), brine (20 ml) and were dried with MgSO$_4$. After the solvent was removed by rotary evaporation bromoiodothiophene **3** was obtained by distillation under vacuum as a yellow liquid (27.25 g, 81%). Bp 105 °C (5 × 10^{-3} mbar); ^{1}H-NMR (CDCl$_3$): $\delta = 6.99$ (s, 1H, 4-H), 2.55 (t, $J = 7.6$ Hz, 2H, α-H), 1.61–1.52 (m, 2H, β-H), 1.28–1.29 (m, 6H, –CH_2–), 0.92 (t, $J = 6.7$ Hz, 3H, –CH_3).

2-(3-Hexyl-thien-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2). To thiophene **1** (4.94 g, 20 mmol) in THF (20 ml) at −80 °C was added n-BuLi (13.2 ml, 21 mmol). After stirring at −80 °C for one hour tri(isopropyl)borate (4.14 g, 22 mmol) was added and the solution was allowed to warm up to room temperature. After an additional two hours at room temperature, pinacol (2.84 g, 24 mmol) was added and the resulting suspension was stirred over night at room temperature. Next, THF was taken off and the residue was dissolved in petrol ether. After the white precipitate was filtered off the resulting solution was filtered over neutral aluminium oxide. The solvent was taken off and the product was dried in vacuum. Dioxaborolane **2** was obtained as a brownish oil (5.4 g, 92%)

yield with a purity of 95% (GC) and was used without further purification. ^{1}H-NMR (CDCl$_3$): $\delta = 7.50$ (d, $J = 4.7$ Hz, 1H, 5-H), 7.04 (d, $J = 4.7$ Hz, 1H, 4-H), 2.91 (t, $J = 7.6$ Hz, 2H, α-H), 1.70–1.53 (m, 2H, β-H), 1.40–1.30 (m, 18H, –CH_2–, –CH_3), 0.91 (t, $J = 6.9$ Hz, 3H, –CH_3); ^{13}C-NMR (CDCl$_3$): $\delta = 154.58, 131.13, 128.17, 119.63, 83.39, 31.64, 31.54, 30.41, 30.00, 28.90, 29.29, 28.83, 27.79 24.67, 22.49, 13.99$; MS (EI): m/z [M$^+$] = 294.

5-Bromo-4,3′-dihexyl-2,2′-bithiophene (4). To a solution of bromoiodothiophene **3** (5.29 g, 18 mmol) in DME (80 ml) [Pd(PPh$_3$)$_4$] (835 mg, 0.72 mmol) was added. After the mixture was stirred for 10 min at room temperature thiophene boronic ester **2** (6.71 g, 18 mmol) and a 1 M aqueous solution of sodium hydrogencarbonate (54 ml) were added. The reaction mixture was refluxed under vigorous stirring for 24 hours. Then it was poured into water (200 ml) and the organic phase was separated while the aqueous phase was extracted with ether (3 times 50 ml). The combined extracts were dried over sodium sulfate and the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography (SiO$_2$, petrol ether) to yield bithiophene **4** (6.7 g, 90%) as a yellow liquid. ^{1}H-NMR (CDCl$_3$): $\delta = 7.18$ (d, $J = 5.2$ Hz, 1H, 5′-H), 6.93 (d, $J = 5.2$ Hz, 1H, 4′-H), 6.81 (s, 1H, 3-H), 2.73 (t, $J = 7.8$ Hz, 2H, α′-H), 2.58 (t, $J = 7.7$ Hz, 2H, α-H), 1.68–1.59 (m, 4H, β,β′-H), 1.40–1.30 (m, 12H, –CH_2–), 0.94–0.89 (m, 6H, –CH_3).

5-(4,3′-Dihexyl-2,2′-bithienyl-5-yl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (10). To bithiophene **4** (1 g, 2.4 mmol) in THF (5 ml) at −80 °C was added n-BuLi (1.6 ml, 2.5 mmol). After stirring at −80 °C for one hour tri(isopropyl)borate (500 mg, 2.7 mmol) was added and the solution was allowed to warm up to room temperature. After an additional two hours at room temperature pinacol (340 g, 2.9 mmol) was added and the resulting suspension was stirred overnight at room temperature. Next, the THF was taken off and the residue was dissolved in petrol ether. After the white precipitate was filtered off the resulting solution was filtrated over neutral aluminium oxide. The solvent was taken off and the product was dried in vacuum. Dioxaborolane **10** was obtained as a brownish oil (1.1 g, 98%) yield with a purity of 95% (GC). It was used without further purification. ^{1}H-NMR (CDCl$_3$): $\delta = 7.14$ (d, $J = 5.2$ Hz, 1H, 5′-H), 7.02 (s, 1H, 3-H), 6.91 (d, $J = 5.2$ Hz, 1H, 4′-H), 2.85 (t, $J = 7.6$ Hz, 2H, α′-H), 2.77 (t, $J = 7.8$ Hz, 2H, α-H), 1.40–1.25 (m, 28H, –CH_2–, –CH_3), 0.93–0.85 (m, 6H, –CH_3); ^{13}C-NMR (CDCl$_3$): $\delta = 154.31, 149.33, 141.32, 139.07, 130.37, 129.32, 128.45, 123.05, 82.90, 31.01, 30.88, 30.24, 30.03, 29.82, 29.63, 28.80, 28.56, 28.50, 28.30, 27.23, 24.12, 21.94, 13.45, 13.41$; MS (EI): m/z [M$^+$] = 460.

5-Bromo-4,3′,3″-trihexyl-2,2′;5,2″-terthiophene (5). Bithiophene **4** (829 mg, 2 mmol) was dissolved in THF (5 ml). At −80 °C n-BuLi (1.32 ml, 2.1 mmol) was added dropwise and the resulting solution was stirred for one hour at −80 °C. After addition of zinc chloride (2.1 mmol as a 1 M solution in THF) the solution was allowed to warm up to room temperature. Next, this reaction mixture was transferred to a solution of 2-bromo-3-hexyl-5-iodothiophene **3** (783.5 mg, 2.1 mmol) and [Pd(PPh$_3$)$_4$] (232 mg, 0.2 mmol) in THF (5 ml) *via* cannula. The resulting orange solution was stirred at room temperature for 24 h under light protection. Then the reaction mixture was poured into water (20 ml) and the organic layer was taken off while the water phase was extracted with dichloromethane (three times 20 ml). The combined organic phases were dried with MgSO$_4$ and the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography (SiO$_2$, petrol ether–dichloromethane 10 : 1). Terthiophene **5** was obtained as an orange viscous liquid (440 mg, 38%). ^{1}H-NMR (CDCl$_3$): $\delta = 7.12$ (d, $J = 5.1$ Hz, 1H, 5″-H), 6.93 (s, 1H, 4′-H), 6.90 (d, $J = 5.2$ Hz, 1H, 4″-H), 6.86 (s, 1H, 3-H), 2.73 (t, $J = 7.8$ Hz, 4H, α′,α″-H), 2.61 (t, $J = 7.8$ Hz, 2H, α-H), 1.67–1.57 (m, 6H,

β–β″-*H*), 1.35–1.25 (m, 18H, –C*H₂*–), 0.94–0.85 (m, 9H, –C*H₃*); ^{13}C-NMR (CDCl₃): δ = 143.53, 139.37, 135.88, 131.02, 129.87, 127.33, 123.38, 121.97, 119.89, 31.71, 31.68, 30.71, 30.53, 30.40, 29.23, 20.17, 29.02, 22.64, 14.10, 14.07; MS (EI): *m/z* [M⁺] = 579; elemental analysis: calcd (%) for C₃₀H₄₃BrS₃: C 62.15, H: 7.48, S: 16.59; found C 62.36, H: 7.42, S: 16.71.

General procedure for the preparation of the perylenyl-oligo-thiophenes (7–9) *via* Negishi cross coupling. To a 0.1 M solution of the bromothiophene in dry THF at −80 °C was added *n*-BuLi (1.02 equivalents). After stirring at −80 °C for one hour zinc chloride (1.05 equivalents, 1 N solution in THF) was added and the solution was allowed to warm up to room temperature. Next, this reaction mixture was transferred to a suspension of PDCI-Br **6** (1.1 equivalents, 1 N solution in THF) and [Pd(PPh₃)₄] (10 mol%) in THF *via* cannula. The resulting red suspension was stirred at 65 °C for 24 h. Then the solvent was taken off and the crude product was purified by flash column chromatography.

2-([*N*-(2,6-Diisopropylphenyl)]-9-perylenyl-3,4-dicarboximide)-3-hexyl-thiophene (7). Following the general procedure, 2-bromo-3-hexylthiophene **1** (136 mg, 0.55 mmol) in THF (10 ml) was converted to the corresponding zincate by subsequently adding *n*-BuLi (0.35 ml, 0.56 mmol) and zinc chloride (82 mg, 0.6 mmol) at −80 °C. The resulting zincate was reacted with 9-bromo-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide **6** (280 mg, 0.5 mmol) and [Pd(PPh₃)₄] (58 mg, 0.05 mmol) to give **7** (200 mg, 62%) as a red solid after flash column chromatography (SiO₂, dichloromethane–petrol ether 2 : 1). Mp 145–146 °C; ^{1}H-NMR (CDCl₃): δ = 8.59 (d, *J* = 8.0 Hz, 2H, *Pery*-1*H*,6*H*), 8.35–8.25 (m, 4H, *Pery*-2*H*,5*H*,7*H*,12*H*), 7.87 (d, *J* = 8.3 Hz, 1H, *Pery*-8*H*), 7.61 (d, *J* = 7.7 Hz, 1H, *Pery*-10*H*), 7.56–7.65 (m, 3H, *Pery*-11*H*, *Ph*-4*H*, *Th*-3*H*), 7.40 (d, *J* = 7.7 Hz, 2H, *Ph*-3*H*,5*H*), 7.16 (d, *J* = 5.2 Hz, 1H, *Th*-4*H*), 2.88 (sep, *J* = 6.8 Hz, 2H, *Ph*-C*H*–(CH₃)₂), 2.48 (t, *J* = 7.6 Hz, 2H, *Th*-α-C*H₂*), 1.60–1.53 (m, 2H, *Th*-β-C*H₂*), 1.29 (d, *J* = 6.8 Hz, 12H, *Ph*-CH–(C*H₃*)₂), 1.35–1.10 (m, 8H, –C*H₂*–), 0.80 (t, *J* = 6.9 Hz, 3H, *Th*-C*H₃*); ^{13}C-NMR (CDCl₃): δ = 162.83, 144.64, 140.46, 136.25, 135.95, 134.37, 132.95, 132.78, 130.81, 130.03, 129.21, 128.41, 128.30, 128.04, 127.97, 127.71, 126.96, 125.98, 125.57, 124.28, 122.98, 122.78, 121.86, 119.85, 119.07, 118.97, 30.42, 29.46, 28.18, 27.86, 23.02, 21.42, 12.94; MS (MALDI-TOF): *m/z* [M + H⁺] = 647; elemental analysis: calcd (%) for C₄₄H₄₁NO₂S: C 81.57, H 6.38, N 2.16; found C 81.79, H 6.57, N 2.17.

5-([*N*-(2,6-Diisopropylphenyl)]-9-perylenyl-3,4-dicarboximide)-4,3′-dihexyl-2,2′-bithiophene (8). Following the general procedure, bithiophene **4** (207 mg, 0.50 mmol) in THF (10 ml) was converted to the corresponding zincate by subsequently adding *n*-BuLi (0.32 ml, 0.51 mmol) and zinc chloride (75 mg, 0.55 mmol) at −80 °C. The resulting zincate was reacted with 9-bromo-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide **6** (308 mg, 0.55 mmol) and [Pd(PPh₃)₄] (58 mg, 0.05 mmol) to give **8** (310 mg, 76%) as a dark red solid after flash column chromatography (SiO₂, dichloromethane–petrol ether 2 : 1). Mp 120–121 °C; ^{1}H-NMR (CDCl₃): δ = 8.65 (d, *J* = 8.0 Hz, 2H, *Pery*-1*H*,6*H*), 8.47–8.38 (m, 4H, *Pery*-2*H*,5*H*,7*H*,12*H*), 8.02 (d, *J* = 8.3 Hz, 1H, *Pery*-8*H*), 7.70 (d, *J* = 7.8 Hz, 1H, *Pery*-10*H*), 7.64 (t, *J* = 7.9 Hz, 1H, *Pery*-11*H*), 7.51 (t, *J* = 7.8 Hz, 1H, *Ph*-4*H*), 7.39 (d, *J* = 7.8 Hz, 2H, *Ph*-3*H*,5*H*), 7.25 (d, *J* = 5.2 Hz, 1H, *Th′*-5*H*), 7.17 (s, 1H, *Th*-3*H*), 7.01 (d, *J* = 5.2 Hz, 1H, *Th′*-4*H*), 2.92–2.80 (m, 4H, *Ph*-C*H*–(CH₃)₂, *Th*-α′-C*H₂*), 2.49 (t, *J* = 7.6 Hz, 2H, *Th*-α-C*H₂*), 1.80–1.70 (m, 2H, *Th*-β′-C*H₂*), 1.66–1.55 (m, 2H, *Th*-β-C*H₂*), 1.51–1.41 (m, 2H, *Th*-γ′-C*H₂*), 1.41–1.31 (m, 4H, *Th*-C*H₂*–), 1.25 (d, *J* = 6.8 Hz, 12H, *Ph*-CH–(C*H₃*)₂), 1.30–1.11 (m, 6H, –C*H₂*–), 0.92 (t, *J* = 6.9 Hz, 3H, *Th′*-C*H₃*), 0.81 (t, *J* = 6.9 Hz, 3H, *Th*-C*H₃*); ^{13}C-NMR (CDCl₃): δ = 168.84, 145.63, 141.75, 139.59, 137.36, 137.09, 136.15, 134.88, 133.80, 133.77, 131.88, 130.99, 130.39, 130.35, 130.25, 130.09, 129.36, 129.22,

129.19, 128.11, 127.30, 127.15, 126.73, 123.93, 123.66, 122.97, 120.98, 120.93, 120.22, 120.14, 31.60, 31.40, 30.63, 30.38, 29.29, 29.17, 29.10, 28.95, 28.83, 23.96, 22.55, 22.40, 14.02, 13.91; MS (MALDI-TOF): *m/z* [M + H⁺] = 813; elemental analysis: calcd (%) for C₅₄H₅₅NO₂S₂: C 79.66, H 6.81, N 1.72; found C 79.62, H 6.95, N 1.76.

5-([*N*-(2,6-Diisopropylphenyl)]-9-perylenyl-3,4-dicarboximide)-4,3′,3″-trihexyl-2,2′;5′,2″-terthiophene (9). Following the general procedure terthiophene **5** (203 mg, 0.35 mmol) in THF (10 ml) was converted into the corresponding zincate by subsequently adding *n*-BuLi (0.22 ml, 0.35 mmol) and zinc chloride (50 mg, 0.37 mmol) at −80 °C. The resulting zincate was reacted with 9-bromo-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide **6** (213 mg, 0.37 mmol) and [Pd(PPh₃)₄] (41 mg, 0.035 mmol) to give **9** (120 mg, 35%) as a black solid after flash column chromatography (SiO₂, dichloromethane–petrol ether 2 : 1). Mp 98–99 °C; ^{1}H-NMR (CDCl₃): δ = 8.68 (d, *J* = 8.0 Hz, 2H, *Pery*-1*H*,6*H*), 8.54–8.49 (m, 4H, *Pery*-2*H*,5*H*,7*H*,12*H*), 8.00 (d, *J* = 8.3 Hz, 1H, *Pery*-8*H*), 7.70 (d, *J* = 7.8 Hz, 1H, *Pery*-10*H*), 7.66 (t, *J* = 7.8 Hz, 1H, *Pery*-11*H*), 7.48 (t, *J* = 7.8 Hz, 1H, 1H, *Ph*-4*H*), 7.34 (d, *J* = 7.8 Hz, 2H, *Ph*-3*H*,5*H*), 7.18 (d, *J* = 5.2 Hz, 1H, *Th′*-5*H*), 7.14 (s, 1H, *Th*-3*H*), 6.98 (s, 1H, *Th′*-4*H*), 6.95 (d, *J* = 5.3 Hz, 1H, *Th′*-4*H*), 2.80–2.65 (m, 6H, *Ph*-C*H*–(CH₃)₂, *Th*-α′,α″-C*H₂*), 2.44 (t, *J* = 7.6 Hz, 2H, *Th*-α-C*H₂*), 1.81–1.65 (m, 4H, *Th*-β′,β″-C*H₂*), 1.65–1.57 (m, 2H, *Th*-β-C*H₂*), 1.57–1.15 (m, 18H, –C*H₂*–), 1.22 (d, *J* = 6.8 Hz, 12H, *Ph*-CH–(C*H₃*)₂), 0.93 (m, 6H, *Th′*,*Th″*-C*H₃*), 0.77 (t, *J* = 6.9 Hz, 3H, *Th*-C*H₃*); ^{13}C-NMR (CDCl₃): δ = 163.88, 145.64, 141.84, 139.74, 139.60, 137.51, 137.24, 135.80, 134.89, 134.14, 133.85, 132.00, 131.97, 130.45, 130.37, 130.30, 130.21, 130.01, 1129.37, 129.35, 129.31, 128.71, 128.19, 127.22, 127.09, 126.85, 123.96, 123.90, 123.55, 123.03, 121.04, 120.97, 120.35, 120.27, 31.57, 31.37, 30.53, 30.46, 30.34, 29.58, 29.38, 29.20, 29.13, 29.11, 29.04, 28.91, 28.79, 23.89, 22.51, 22.36, 13.97, 13.87; MS (MALDI-TOF): *m/z* [M + H⁺] = 979; elemental analysis: calcd (%) for C₆₄H₆₉NO₂S₃: C 78.40, H 7.09, N 1.43; found C 78.61, H: 7.26, N: 1.34.

General procedure for the preparation of perylenyl-oligo-thiophenes (8,12,14,16) *via* Suzuki coupling. To a solution of the halogenated compound (1 equivalent) in DME [Pd(PPh₃)₄] (5 mol%) and dioxaborolane **10** (1.2 equivalents) were added. After addition of a 2 M aqueous solution of tripotassium phosphate (2 equivalents) the mixture was stirred for 3 hours at 60 °C. Next, it was poured into water and the organic phase was separated while the aqueous phase was extracted with dichloromethane. The combined extracts were dried over sodium sulfate and the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography and was dried in vacuum.

General procedure for the preparation of iodinated perylenyl-oligothiophenes (11,13,15). To a solution of the perylenyl-oligothiophene (1 equivalent) in dry dichloromethane was added mercury caproate (1.01 equivalents). The resulting suspension was stirred at room temperature until the mercury compound was completely dissolved. Next, iodine (1.1 equivalents) was added and the mixture was stirred for another six hours. Then the solution was filtered over basic aluminium oxide and the filtrate was concentrated in vacuum. Upon addition of ethanol the product was allowed to precipitate, was filtered and dried in vacuum.

5-([*N*-(2,6-Diisopropylphenyl)]-9-perylenyl-3,4-dicarboximide)-4,3′-dihexyl-2,2′-bithiophene (8). Following the general procedure, 9-bromo-*N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide **6** (2.5 g, 4.5 mmol), dioxaborolane **10** (2.5 g, 5.5 mmol), tripotassium phosphate (5.5 ml, 11 mmol) and [Pd(PPh₃)₄] (260 mg, 0.225 mmol) in DME (30 ml) were reacted at 80 °C for 3 hours to give **8** (3.3 g, 90%) as a dark red solid after flash column chromatography (SiO₂, dichloromethane–petrol

ether 2 : 1). Mp 120–121 °C; same spectroscopic and analytical data as described above for Negishi coupling.

5-([*N*-(2,6-Diisopropylphenyl)]-9-perylenyl-3,4-dicarboximide)-4,3′-dihexyl-5′-iodo-2,2′-bithiophene (11). Following the general procedure perylenyl-bithiophene **8** (2.85 g, 3.5 mmol), mercury capronate (1.52 mg, 3.54 mmol) and iodine (977 mg, 3.85 mmol) in dichloromethane (17 ml) were reacted to give **11** (3.2 g, 97%) as a red solid. Mp 124–125 °C; ^{1}H-NMR (CDCl$_3$): δ = 8.65 (d, J = 8.0 Hz, 2H, *Pery*-1*H*,6*H*), 8.47–8.38 (m, 4H, *Pery*-2*H*,5*H*,7*H*,12*H*), 7.99 (d, J = 8.3 Hz, 1H, *Pery*-8*H*), 7.70–7.62 (m, 2H, *Pery*-10H,11H), 7.52 (t, J = 7.8 Hz, 1H, *Ph*-4*H*), 7.39 (d, J = 7.8 Hz, 2H, *Ph*-3*H*,5*H*), 7.14 (s, 1H, *Th′*-4*H*), 7.10 (s, 1H, *Th*-3*H*), 2.90–2.80 (m, 4H, *Ph*–CH–(CH$_3$)$_2$, *Th*–α′-CH$_2$), 2.47 (t, J = 7.6 Hz, 2H, *Th*–α-CH$_2$), 1.75–1.65 (m, 2H, *Th*–β′-CH$_2$), 1.65–1.54 (m, 2H, *Th*–β-CH$_2$), 1.51–1.41 (m, 2H, *Th*–γ-CH$_2$), 1.47–1.29 (m, 4H, –CH$_2$–), 1.24 (d, J = 6.8 Hz, 12H, *Ph*–CH–(CH$_3$)$_2$), 1.29–1.11 (m, 6H, –CH$_2$–), 0.92 (t, J = 6.9 Hz, 3H, *Th′*–CH$_3$), 0.80 (t, J = 6.9 Hz, 3H, *Th*–CH$_3$); ^{13}C-NMR (CDCl$_3$): δ = 162.89, 144.68, 140.90, 140.43, 138.86, 136.39, 136.10, 135.51, 133.74, 133.61, 133.49, 132.79, 130.95, 130.02, 129.42, 129.32, 128.42, 128.39, 128.35, 127.19, 126.73, 126.28, 125.80, 122.99, 122.01, 120.12, 120.05, 119.35, 119.27, 70.63, 30.60, 30.44, 29.59, 29.40, 28.15, 28.13, 28.00, 27.97, 27.87, 23.02, 21.57, 21.44, 13.06, 12.97; MS (MALDI-TOF): m/z [M + H$^+$] = 939; elemental analysis: calcd (%) for C$_{54}$H$_{54}$INO$_2$S$_2$: C 69.00, H 5.74, N 1.49; found C 69.15, H 5.79, N 1.36.

5-([*N*-(2,6-Diisopropylphenyl)]-9-perylenyl-3,4-dicarboximide)-4,3′,3″,3‴-tetrahexyl-2,2′;5′,2″;5″,2‴-quaterthiophene (12). Following the general procedure iodinated perylenyl-bithiophene **11** (1.4 g, 1.5 mmol), dioxaborolane **10** (800 mg, 1.7 mmol), tripotassium phosphate (1.7 ml, 3.4 mmol) and [Pd(PPh$_3$)$_4$] (87 mg, 0.075 mmol) in DME (10 ml) were reacted at 80 °C for 3 hours to give **12** (1.4 g, 82%) as a black solid after flash column chromatography (SiO$_2$, dichloromethane–petrol ether 2 : 1). Mp 89–90 °C; ^{1}H-NMR (CDCl$_3$): δ = 8.64 (d, J = 8.0 Hz, 2H, *Pery*-1*H*,6*H*), 8.49–8.42 (m, 4H, *Pery*-2*H*,5*H*,7*H*,12*H*), 8.00 (d, J = 8.3 Hz, 1H, *Pery*-8*H*), 7.68 (d, J = 7.8 Hz, 1H, *Pery*-10*H*), 7.63 (t, J = 7.9 Hz, 1H, *Pery*-11*H*), 7.48 (t, J = 7.8 Hz, 1H, *Ph*-4*H*), 7.34 (d, J = 7.8 Hz, 2H, *Ph*-3*H*,5*H*), 7.17–7.15 (m, 2H, *Th*-3*H*, *Th‴*-5*H*), 7.00 (s, 1H, *Th′*-4*H*), 6.96 (s, 1H, *Th″*-4*H*), 6.93 (d, J = 5.3 Hz, 1H, *Th‴*-4*H*), 2.87–2.75 (m, 8H, *Ph*–CH–(CH$_3$)$_2$, *Th*–α′,α″-CH$_2$), 2.45 (t, J = 7.6 Hz, 2H, *Th*–α-CH$_2$), 1.70–1.60 (m, 6H, *Th*–β′,β″-CH$_2$), 1.60–1.50 (m, 2H, *Th*–β-CH$_2$), 1.50–1.22 (m, 24H, –CH$_2$–), 1.20 (d, J = 6.8 Hz, 12H, *Ph*–CH–(CH$_3$)$_2$), 0.96–0.82 (m, 9H, *Th′*–*Th‴*–CH$_3$), 0.79 (t, J = 6.9 Hz, 3H, *Th*–CH$_3$); ^{13}C-NMR (CDCl$_3$): δ = 163.96, 145.74, 141.97, 139.87, 139.67, 137.54, 137.26, 135.91, 134.95, 134.22, 134.01, 133.94, 133.91, 132.05, 131.08, 130.51, 130.39, 130.35, 130.12, 129.41, 129.38, 128.79, 128.63, 128.28, 127.31, 127.22, 126.91, 124.02, 123.65, 123.11, 121.14, 121.08, 120.41, 120.32, 31.71, 31.50, 30.65, 30.59, 30.52, 30.48, 29.53, 29.48, 29.28, 29.26, 29.24, 29.18, 29.05, 28.94, 24.04, 22.65, 22.50, 14.11; MS (MALDI-TOF): m/z [M + H$^+$] = 1145; elemental analysis: calcd (%) for C$_{74}$H$_{83}$NO$_2$S$_4$: C 77.51, H 7.30, N 1.22; found C 77.45, H 7.28, N 1.00.

5-([*N*-(2,6-Diisopropylphenyl)]-9-perylenyl-3,4-dicarboximide)-4,3′,3″,3‴-tetrahexyl-5‴-iodo-2,2′;5′,2″;5″,2‴-quaterthiophene (13). Following the general procedure perylenyl-quaterthiophene **12** (800 mg, 0.7 mmol), mercury capronate (304 mg, 0.71 mmol) and iodine (195 mg, 0.77 mmol) in dichloromethane (4 ml) were reacted to give **13** (825 mg, 93%) as a black solid. Mp 97–98 °C; ^{1}H-NMR (CDCl$_3$): δ = 8.62 (d, J = 8.0 Hz, 2H, *Pery*-1*H*,6*H*), 8.45–8.35 (m, 4H, *Pery*-2*H*,5*H*,7*H*,12*H*), 7.98 (d, J = 8.4 Hz, 1H, *Pery*-8*H*), 7.66 (d, J = 7.8 Hz, 1H, *Pery*-10*H*), 7.61 (t, J = 7.9 Hz, 1H, *Pery*-11*H*), 7.48 (t, J = 7.8 Hz, 1H, *Ph*-4*H*), 7.35 (d, J = 7.8 Hz, 2H, *Ph*-3*H*,5*H*), 7.16 (s, 1H, *Th*-3*H*), 7.05 (s, 1H, *Th′*-4*H*), 7.00 (s, 1H, *Th″*-4*H*), 6.89

(s, 1H, *Th‴*-4*H*), 2.90–2.70 (m, 8H, *Ph*–CH–(CH$_3$)$_2$, *Th*–α′,α‴-CH$_2$), 2.45 (t, J = 7.6 Hz, 2H, *Th*–α-CH$_2$), 1.80–1.65 (m, 6H, *Th*–β′–β‴-CH$_2$), 1.65–1.50 (m, 2H, *Th*–β-CH$_2$), 1.50–1.05 (m, 24H, –CH$_2$–), 1.21 (d, J = 6.8 Hz, 12H, *Ph*–CH–(CH$_3$)$_2$), 0.97–0.81 (m, 9H, *Th′*–*Th‴*–CH$_3$), 0.77 (t, J = 6.9 Hz, 3H, *Th*–CH$_3$); ^{13}C-NMR (CDCl$_3$): δ = 163.92, 145.71, 141.97, 141.40, 139.95, 139.87, 137.43, 137.16, 136.53, 135.81, 134.86, 134.08, 133.84, 133.61, 132.67, 131.97, 131.06, 130.92, 130.59, 130.45, 130.35, 129.44, 129.34, 129.13, 128.78, 128.22, 127.27, 126.82, 124.01, 123.06, 121.10, 121.04, 120.34, 120.26, 71.53, 31.68, 31.62, 31.49, 30.55, 30.48, 29.52, 29.43, 29.28, 29.23, 29.18, 29.13, 29.05, 28.97, 28.93, 24.04, 22.64, 22.60, 22.49, 14.11, 14.00; MS (MALDI-TOF): m/z [M + H$^+$] = 1271; elemental analysis: calcd (%) for C$_{74}$H$_{82}$INO$_2$S$_4$: C 69.89, H 6.49, N 1.10; found C 70.05, H 6.52, N 0.92.

5-([*N*-(2,6-Diisopropylphenyl)]-9-perylenyl-3,4-dicarboximide)-4,3′,3″,3‴,3″″,3‴″-hexahexyl-2,2′;5′,2″;5″,2‴;5‴,2″″;5″″,2‴″-sexithiophene (14). Following the general procedure iodinated perylenyl-quaterthiophene **13** (160 mg, 126 μmol), dioxaborolane **10** (70 mg, 151 μmol), tripotassium phosphate (0.15 ml, 302 μmol) and [Pd(PPh$_3$)$_4$] (153 mg, 13 μmol) in DME (1 ml) were reacted at 60 °C for 4 hours to give **14** (140 mg, 75%) as a black solid after flash column chromatography (SiO$_2$, dichloromethane–petrol ether 2 : 1). Mp 64–65 °C; ^{1}H-NMR (CDCl$_3$): δ = 8.65 (d, J = 8.0 Hz, 2H, *Pery*-1*H*,6*H*), 8.52 − 8.40 (m, 4H, *Pery*-2*H*,5*H*,7*H*,12*H*), 8.00 (d, J = 8.3 Hz, 1H, *Pery*-8*H*), 7.69 (d, J = 7.8 Hz, 1H, *Pery*-10*H*), 7.63 (t, J = 7.9 Hz, 1H, *Pery*-11*H*), 7.48 (t, J = 7.8 Hz, 1H, *Ph*-4*H*), 7.35 (d, J = 7.8 Hz, 2H, *Ph*-3*H*,5*H*), 7.16 (m, 2H, *Th*-3*H*, *Th″″*-5*H*), 7.1–6.90 (m, 5H, *Th′*–*Th″″*-4*H*), 2.90–2.75 (m, 12H, *Ph*–CH–(CH$_3$)$_2$, *Th*–α′–α″″-CH$_2$), 2.46 (t, J = 7.5 Hz, 2H, *Th*–α-CH$_2$), 1.80–1.50 (m, 24H, –CH$_2$–), 1.50–1.10 (m, 24H, –CH$_2$–), 1.20 (d, J = 6.8 Hz, 12H, *Ph*–CH–(CH$_3$)$_2$), 0.95–0.80 (m, 15H, *Th′*–*Th‴*–CH$_3$), 0.78 (t, J = 6.9 Hz, 3H, *Th*–CH$_3$); ^{13}C-NMR (CDCl$_3$): δ = 163.85, 145.65, 141.88, 139.85, 139.80, 139.72, 139.55, 137.47, 137.20, 135.79, 134.85, 134.05, 133.93, 133.84, 133.80, 133.75, 131.94, 130.97, 130.44, 130.41, 130.31, 130.29, 130.26, 129.99, 129.36, 129.32, 128.68, 128.49, 128.20, 127.22, 127.13, 126.85, 123.95, 123.89, 123.49, 123.01, 121.07, 121.01, 120.34, 120.26, 31.59, 31.57, 31.37, 30.53, 30.46, 30.40, 30.35, 29.42, 29.38, 29.20, 29.16, 29.13, 29.11, 29.06, 28.81, 23.91, 22.53, 22.49, 22.37, 13.99, 13.97, 12.67; MS (MALDI-TOF): m/z [M + H$^+$] = 1478; elemental analysis: calcd (%) for C$_{94}$H$_{111}$NO$_2$S$_6$: C 76.32, H 7.65, N 0.95; found C 76.36, H 7.70, N 0.90.

5-([*N*-(2,6-Diisopropylphenyl)]-9-perylenyl-3,4-dicarboximide)-4,3′,3″,3‴,3″″,3‴″-hexahexyl-5‴″-iodo 2,2′;5′,2″;5″,2‴;5‴,2″″;5″″,2‴″-sexithiophene (15). Following the general procedure perylenyl-sexithiophene **14** (210 mg, 0.14 mmol), mercury caproate (62 mg, 0.14 mmol) and iodine (40 mg, 0.16 mmol) in dichloromethane (5 ml) were reacted to give **15** (210 mg, 94%) as a black solid. Mp 76–77 °C; ^{1}H-NMR (CDCl$_3$): δ = 8.65 (d, J = 8.0 Hz, 2H, *Pery*-1*H*,6*H*), 8.52–8.40 (m, 4H, *Pery*-2*H*,5*H*,7*H*,12*H*), 8.00 (d, J = 8.3 Hz, 1H, *Pery*-8*H*), 7.69 (d, J = 7.8 Hz, 1H, *Pery*-10*H*), 7.63 (t, J = 7.9 Hz, 1H, *Pery*-11*H*), 7.48 (t, J = 7.8 Hz, 1H, *Ph*-4*H*), 7.35 (d, J = 7.8 Hz, 2H, *Ph*-3*H*,5*H*), 7.16 (s, 1H, *Th*-3*H*), 7.06 (s, 1H, *Th′*-4*H*), 7.02 (s, 1H, *Th″*-4*H*), 6.99 (s, 1H, *Th‴*-4*H*), 6.96 (s, 1H, *Th*-4″″*H*), 6.88 (s, 1H, *Th″″*-4*H*), 2.90–2.75 (m, 12H, *Ph*–CH–(CH$_3$)$_2$, *Th*–α′–α″″-CH$_2$), 2.46 (t, J = 7.5 Hz, 2H, *Th*–α-CH$_2$), 1.80–1.50 (m, 24H, –CH$_2$–), 1.50–1.10 (m, 24H, –CH$_2$–), 1.20 (d, J = 6.8 Hz, 12H, *Ph*–CH–(CH$_3$)$_2$), 0.95–0.80 (m, 15H, *Th′*–*Th″″*–CH$_3$), 0.78 (t, J = 6.9 Hz, 3H, *Th*–CH$_3$); ^{13}C-NMR (CDCl$_3$): δ = 163.66, 145.45, 141.12, 139.66, 139.53, 137.26, 136.99, 136.27, 135.57, 134.64, 133.75, 133.63, 133.56, 133.45, 133.22, 132.33, 131.74, 130.78, 130.68, 130.34, 130.24, 130.09, 129.12, 128.86, 128.47, 128.36, 128.00, 127.01, 126.94, 126.64, 123.75, 123.70, 122.81, 120.87, 120.80, 120.14, 120.05, 71.15, 31.39, 31.31, 31.18, 30.25, 30.19, 30.16, 29.22, 29.18,

29.09, 28.95, 28.90, 28.86, 28.81, 28.73, 28.65, 28.61, 23.71, 22.33, 22.28, 22.17, 13.79, 13.70; MS (MALDI-TOF): m/z [M + H$^+$] = 1604; elemental analysis: calcd (%) for $C_{94}H_{110}INO_2S_6$: C 70.34, H 6.91, N 0.87; found C 70.50, H 6.79, N 0.92.

5-([N-(2,6-Diisopropylphenyl)]-9-perylenyl-3,4-dicarboximide)-4,3′,3″,3‴,3⁗,3‴″,3⁗″ - octaahexyl - 2,2′;5′,2″;5″,2‴;5‴,2⁗;5⁗,2‴″;5‴″,2⁗″;5⁗″,2‴‴-octathiophene (16). Following the general procedure iodinated perylenyl-sexithiophene **15** (25 mg, 16 µmol), dioxaborolane **10** (9 mg, 19 µmol), tripotassium phosphate (19 µl, 38 µmol) and [Pd(PPh$_3$)$_4$] (2 mg, 1.6 µmol) in DME (0.5 ml) were reacted at 60 °C for 4 hours to give **16** (20 mg, 70%) as a black solid after flash column chromatography (SiO$_2$, dichloromethane–petrol ether 2 : 1). Mp 66–67 °C; ^{1}H-NMR (CDCl$_3$): δ = 8.70 (d, J = 8.0 Hz, 2H, *Pery*-1*H*,6*H*), 8.56–8.50 (m, 4H, *Pery*-2*H*,5*H*,7*H*,12*H*), 8.04 (d, J = 8.4 Hz, 1H, *Pery*-8*H*), 7.75 − 7.65 (m, 2H, *Pery*-10*H*,11*H*), 7.51 (t, J = 7.8 Hz, 1H, *Ph*-4*H*), 7.37 (d, J = 7.7 Hz, 2H, *Ph*-3*H*,5*H*), 7.20–7.15 (m, 2H, *Th*-3*H*, *Th*-5⁗″*H*), 7.12–6.95 (m, 7H, *Th′–Th*–⁗‴4*H*), 2.90–2.75 (m, 16H, *Ph–CH*–(CH$_3$)$_2$, *Th*–α′–α⁗″–CH$_2$), 2.48 (t, J = 7.5 Hz, 2H, *Th*–α-CH$_2$), 1.80–1.55 (m, 16H, –CH$_2$–), 1.55–1.10 (m, 48H, –CH$_2$–), 1.22 (d, J = 6.8 Hz, 12H, *Ph*–CH–(CH$_3$)$_2$), 0.97–0.85 (m, 21H, *Th′–Th*⁗‴–CH$_3$), 0.81 (t, J = 6.9 Hz, 3H, *Th*–CH$_3$); ^{13}C-NMR (CDCl$_3$): δ = 161.79, 143.59, 139.82, 137.79, 137.76, 137.65, 137.48, 135.41, 135.14, 133.73, 132.79, 131.88, 131.79, 131.74, 131.65, 129.90, 129.88, 128.92, 128.38, 128.26, 128.23, 127.92, 127.34, 127.30, 127.27, 126.62, 126.43, 126.15, 125.15, 125.07, 124.79, 121.89, 121.83, 121.43, 120.95, 119.02, 118.96, 118.28, 118.20, 29.53, 29.32, 28.47, 28.41, 28.33, 28.29, 27.36, 27.31, 27.14, 27.09, 27.05, 27.00, 26.87, 26.75, 21.85, 20.48, 20.47, 20.43, 20.31, 11.93, 11.81; MS (MALDI-TOF): m/z [M + H$^+$] = 1810; elemental analysis: calcd (%) for $C_{144}H_{139}NO_2S_8$: C 75.57, H 7.73, N 0.77; found C 75.65, H 7.79, N 0.85.

Acknowledgements

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