Perylene–Oligothiophene–Perylene Triads for Photovoltaic Applications

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A series of novel acceptor–donor–acceptor triad systems, consisting of head-to-tail-coupled oligo(3-hexylthiophene)s integrated between two terminal perylenemonoimides are described. These hybrid molecules, which differ by the length of the oligothiophene units from a quaterthiophene up to a dodecithiophene were synthesized by an effective palladium-catalyzed Ullmann-type homo-coupling reaction in good yields. The optical and electrochemical properties of these compounds were determined, and on the basis of this series structure-property relationships have been established which provide vital information for the fabrication of the corresponding 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

Donor–acceptor molecules are attractive systems in that they are considered to be promising for applications in molecular and supramolecular electronics, light harvesting, photocatalysis and especially to find important applications in organic photovoltaic cells to convert sunlight into electrical energy.[1] The field of organic photovoltaics has made tremendous progress over the last ten years accompanied by a rapid increase in energy conversion efficiency.[2] Nevertheless, as energy conversion efficiencies are still far from their inorganic counterparts, an industrial production of organic solar cells is not yet economical. Their lower efficiency is mainly related to the low optical absorbance within the terrestrial sun spectrum and the moderate charge carrier mobilities of the photoactive layer. One promising approach to increasing the overall energy conversion efficiencies of organic solar cells is the utilization of a donor–acceptor system, consisting of *n*-type and *p*-type conducting materials, which absorb at different regions within the visible light spectrum and therefore, cover the terrestrial sun spectrum to a great extent. Furthermore, for the manufacturing of efficient and long-living organic solar cells it is necessary to use UV- and thermally stable materials with good electron and hole conductivities.

In this respect, we recently combined the outstanding electronic properties and thermal stability of perylene dyes[3] with those of structurally defined oligothiophenes[4] in order to synthesize a series of perylene-functionalized head-to-tail-coupled oligo(3-hexylthiophene)s as novel donor–acceptor dyads for photovoltaic applications.[5] On the basis of their optical and electrochemical characterization, structure-property relationships have been established which showed the typical dependence of the physical properties on the inverse of the oligomer chain length, allowing for the deduction of valuable information necessary for the fabrication of photovoltaic devices.

It has been demonstrated that the concept of a linear arrangement of π-donor and π-acceptor can be extended to a triad system where the donor is integrated between two terminal acceptor units. As model compounds for this type of hybrid system, perylenyl end-capped oligo- and polyfluorenes have been reported which show photo-induced intramolecular energy transfer between the fluorene and the perylene moieties in the solid state.[6] In analogy, we adapted our original conception of linearly arranged perylenyl-oligothiophenes in a sense that the oligothiophene donor moieties are located in between two terminal perylene acceptor units.

Here, we report the synthesis of a series of triad-like bis(perylenyl)-oligothiophenes (**2**, **4**, and **6**). The optical and electrochemical properties were investigated to show their dependence on the oligothiophene chain length which varies from four to twelve thiophene units and they are compared to dimeric perylenedicarboximide ($PDCI_2$). The novel type of π-acceptor–π-donor–π-acceptor triad system was designed in such a way that the oligothiophene part preserves its typical charge-transport and self-assembling properties in the solid state, and the perylene units, *N*-(2,6-diisopropylphenyl)perylene-3,4-dicarboximide, provide high absorptivity in the visible region as well as electron-accepting properties. With respect to the range of absorption,

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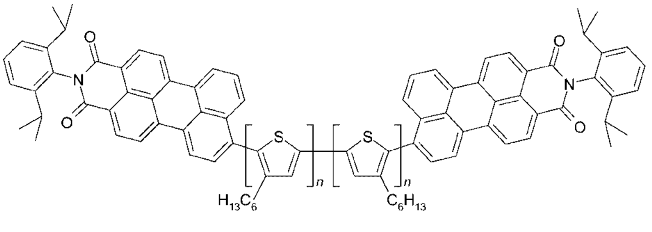
to the energy levels of the frontier orbitals and bands in the solid state, respectively, tailored materials for applications in photovoltaic devices are expected from our novel hybrid molecules.



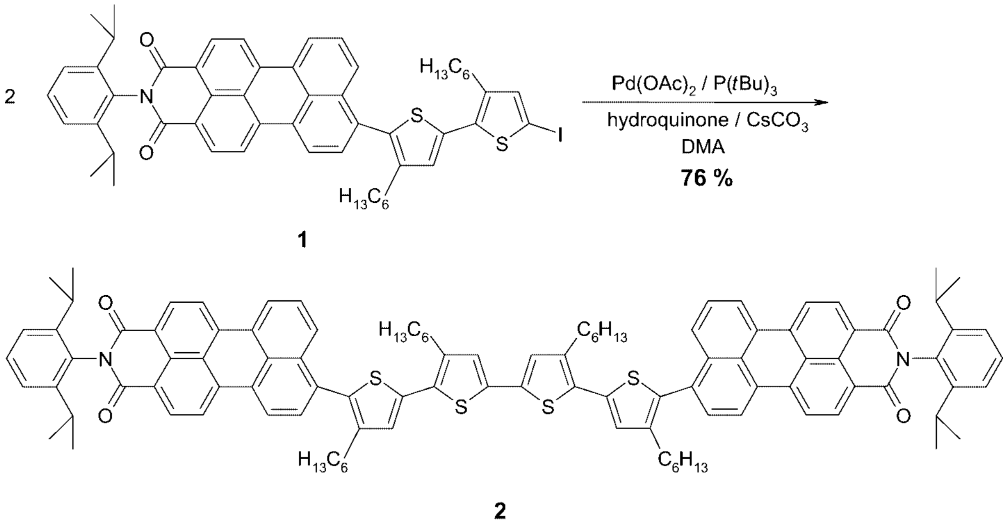
(PDCI)$_2$ (n = 0); **2** (n = 2); **4** (n = 4); **6** (n = 6)

Results and Discussion

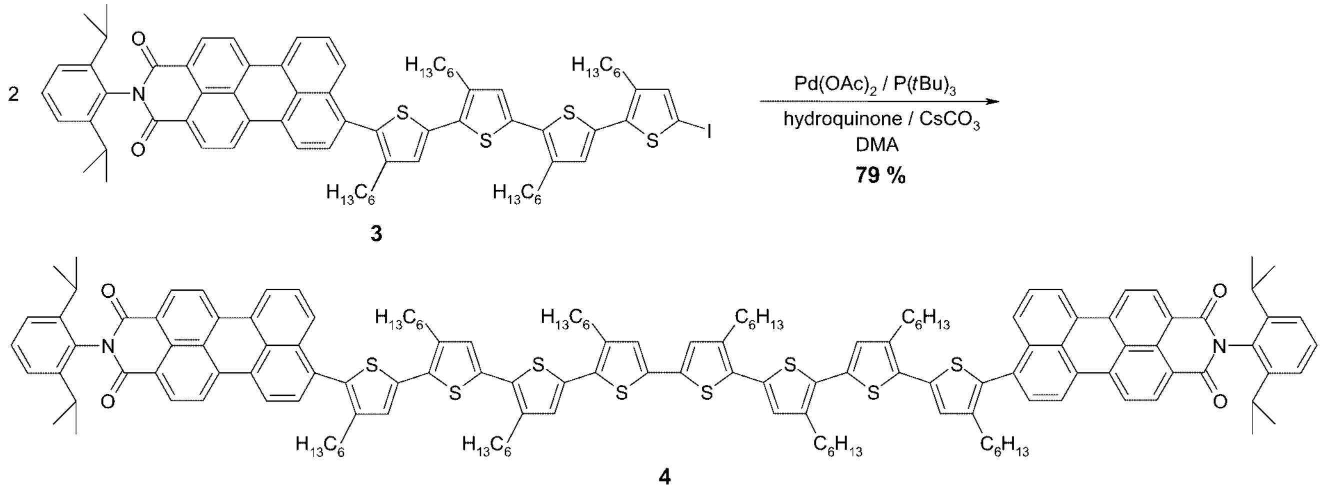
Synthesis

In the series of perylene-functionalized head-to-tail-coupled oligo(3-hexylthiophene)s, the iodinated perylenyl-oligothiophenes **1**, **3**, and **5** were employed as intermediate products for the elongation of the oligothiophene chain and were accessible through an effective mercury-mediated iodiation procedure.[5] We utilized the iodinated perylenyl-oligothiophenes **1**, **3**, and **5** as starting materials for an optimized palladium-catalyzed Ullmann reaction, furnishing the dimeric bis(perylenyl)-oligothiophenes **2**, **4**, and **6** in good to excellent yields.

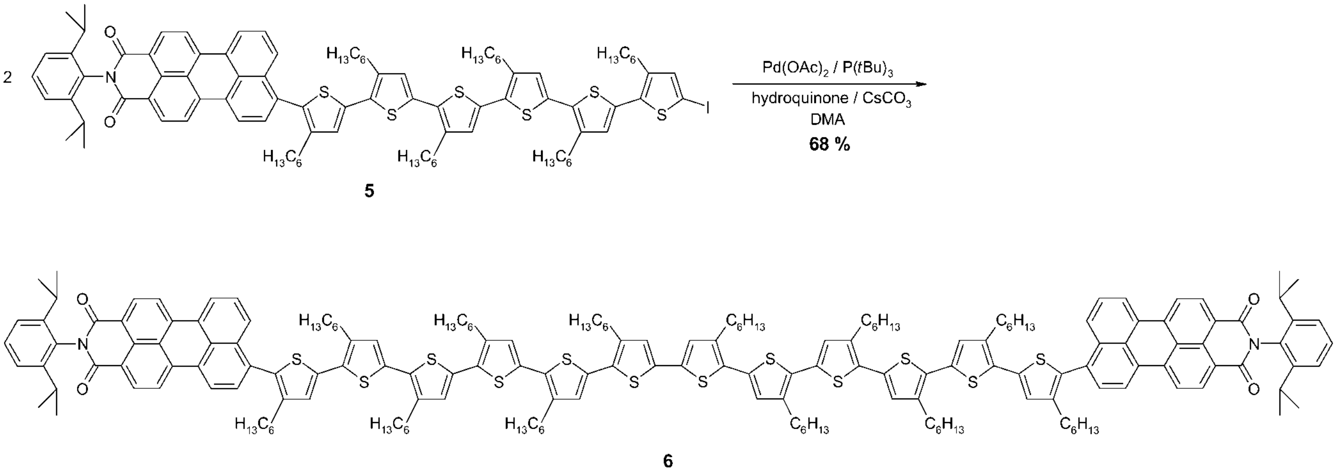
It has been reported in the literature that palladium acetate with tri(*o*-tolyl)phosphane as the ligand and hydroquinone as the oxidant gives excellent yields for the homo-coupling of aryl iodides and bromides.[7] We adapted this strategy and developed a general protocol which has been applied for the dimerization of the iodinated perylenyl-oligothiophenes **1**, **3**, and **5**. We found that the replacement of tri(*o*-tolyl)phosphane by tri(*tert*-butyl)phosphane as the ligand resulted in a more active catalytic system, known to increase the efficiency of various palladium-catalyzed reactions.[8] With the general homo-coupling protocol, bis(perylenyl)-oligothiophenes **2** (n = 2), **4** (n = 4), and **6** (n = 6)



Scheme 1. Homo-coupling of iodinated perylenyl-bithiophene **1** to triad **2**.



Scheme 2. Homo-coupling of iodinated perylenyl-quaterthiophene **3** to triad **4**.



Scheme 3. Homo-coupling of iodinated perylenyl-quaterthiophene **5** to triad **6**.

became accessible in good yields which is depicted in Schemes 1, 2 and 3 and accordingly, the smallest representative of this series bis(perylenyl)-quaterthiophene **2** has been obtained in 76% yield (Scheme 1).

According to this procedure, the next higher homologue, bis(perylenyl)-octithiophene **4**, was obtained in 79% yield by palladium-catalyzed dimerization of iodinated perylenyl-quaterthiophene **3** (Scheme 2).

In the case of the longest analogue, bis(perylenyl)-dodecithiophene **6**, the yield of the dimerization of iodinated derivative **5** was slightly lower (68%), which can be attributed to the partial deiodination of the starting material during exposure to the elevated reaction temperature of 80 °C. In summary, we could effectively synthesize a novel series of linear π-acceptor–π-donor–π-acceptor triads with extensions up to ca. 7 nm in length (Scheme 3).

Electronic Properties

In the homologous series of oligomers, their properties can be investigated as a function of chain length, which furnishes clear structure-property relationships. In this respect, it has been shown experimentally and theoretically that the (electronic) properties of conjugated oligomeric systems linearly depend on the inverse chain length.[9] For the series of bis(perylenyl)-oligothiophenes **2**, **4**, and **6**, 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 series are given in Table 1 and compared to the separately synthesized parent building blocks. The energy gaps were determined from the onset of the longest wavelength absorption band of the hybrid molecules. For comparison, dimeric perylene monoimide PDCI$_2$ was chosen as the reference, consisting of perylene monoimide molecules covalently linked at the 9-position.[11] Additionally, a comparison to the structurally related nonfunctionalized head-to-tail-coupled oligo(3-hexylthiophene)s (HT-O3HTs) is worthwhile, although it has to be considered that the donor units of **2**, **4**, and **6** are not perfect copies of the comparable HT-O3HTs, because in the hybrid systems the oligothiophene moieties are not fully head-to-tail-coupled. Nevertheless, their electronic properties should be very similar due to lacking steric interactions between adjacent thiophene units.

The reference compound PDCI$_2$ shows an intense and structured π–π* transition band in the region of 400–570 nm with a maximum absorption at 529 nm and a shoulder at 501 nm, reflecting a rather planar and rigid aromatic

Table 1. Optical properties of bis(perylenyl)-oligothiophenes **2**, **4**, **6** in CHCl$_3$ solution (c = 5×10^{-5} mol/L) and in the solid state in comparison to PDCI$_2$. P denotes perylene, OT oligothiophene.

Chromophore	λ^{abs}_1 (P) [nm]	log ε	λ^{abs}_2 (OT) [nm]	log ε	λ^{abs}_3 (P) [nm][a] Solution	log ε	$\Delta E_{opt.}$ [eV]	λ^{em} [nm][a]	φ^{em} [%][b]	λ^{abs}_2 (OT) [nm]	λ^{abs}_3 (P) [nm][a] Solid state	ΔE_{opt} [eV]
PDCI$_2$	265	4.72			501,529	4.93	2.18	598	81			
2 (4T)	266	4.84	380[c] (*371*)[d]	4.33	502,523	4.93	2.12	671	2 (*13*)[d]	448[c] (*494*)[d]	497,525	2.01
4 (8T)	266	4.89	428[c] (*422*)[e]	4.74	498,517	4.97	2.11	610	1 (*13*)[e]	477[c] (*560*)[e]	494, 518	2.01
6 (12T)	266	4.95	434[c] (*436*)[f]	4.92	492, 515	5.03	2.11	593	1 (*38*)[f]	481[c] (*579*)[f]	496, 519	2.01

[a] Maxima underlined. [b] Excitation wavelength λ^{ex} = 480 nm. [c] Determined by difference spectra. [d] For comparison values for the comparable nonfunctionalized tetrahexyl-quaterthiophene. [e] Octahexyl-octithiophene. [f] Dodecahexyl-dodecithiophene are given in parentheses.[10]

system (Figure 1). Furthermore, a second band arises below 280 nm (λ_{max} = 265 nm) and a weak third one around 350 nm. The insertion of oligothiophene units between the parent perylene units significantly changes the shape of the perylene band. Although a marginally blue-shift by 6–14 nm of the longest wavelength absorption is observed with respect to the reference compound $PDCI_2$, an increased tendency to a tailing on the low energy side of the band with growing oligothiophene chain length is clearly visible. In the same manner, the optical bandgap of 2.18 eV in the case of the reference compound $PDCI_2$ is gradually diminished to 2.12 eV on going to the quaterthiophene **2** and finally ends up with a bandgap of 2.11 eV for octithiophene **4** and dodecithiophene **6**. The progressive decrease of the optical bandgap with elongation of the adjacent-oligothiophene chain has also been observed for the parent linear perylenyl-oligothiophenes. The tailing and broadening of the band can be attributed to a charge-transfer (CT) transition.[5]

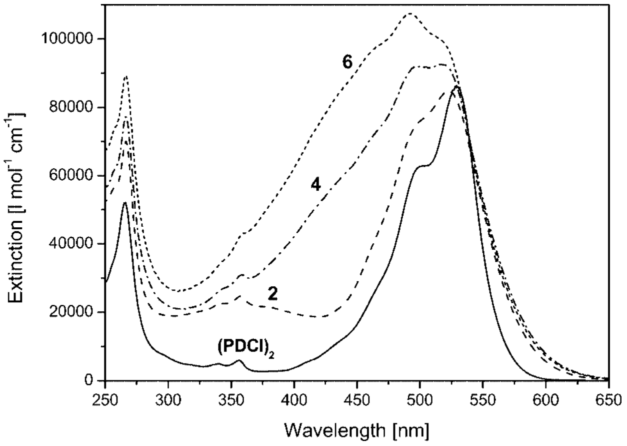


Figure 1. UV/Vis spectra of the bis(perylenyl)-oligothiophenes **2**, **4**, and **6** and reference compound $PDCI_2$ in chloroform (c = 5×10^{-5} mol/L).

The bis(perylenyl)-oligothiophenes **2**, **4**, and **6** show high absorptivities from 300 to 450 nm which can be attributed to the absorption of the oligothiophene moieties. Although no distinct absorption maxima for the donor units are observed, they can be extracted by difference spectra with respect to the parent compound $PDCI_2$ (not shown). The corresponding absorption maxima are calculated to λ = 380 nm for quaterthiophene **2** to λ = 428 nm for octithiophene **4** and to λ = 434 nm for dodecithiophene **6**, revealing the same trend observed for the comparable HT-O3HTs as the absorption becomes red-shifted with increasing length of the oligothiophene subunits.[10] The absorption maxima and the corresponding extinction coefficients are in good agreement with those of the nonfunctionalized HT-O3HTs, indicating that the donor and the acceptor moieties are rather electronically decoupled. Especially in the case of dodecitiophene **6** the values are in perfect match, as a result of a diminished electronic influence of the two perylene moieties on the electronic properties of the oligothiophene unit.

Thin films of bis(perylenyl)-oligothiophenes **2**, **4**, and **6** (thicknesses 40–70 nm) were obtained by spin-coating of the corresponding toluene solutions (c = 20 mg/ml) onto glass substrates (Figure 2). The absorption spectra of **2**, **4**, and **6** in the solid state show the same trends compared to the solution spectra; however, in general a broadening and red-shift of the bands is visible leading to smaller bandgaps (by 0.10 eV). Although only a marginal displacement is observed for the absorption band of the perylene moieties by going from the solution to the solid state, the displacement is significantly greater for the corresponding oligothiophene absorption maxima which depend on the oligothiophene chain length.

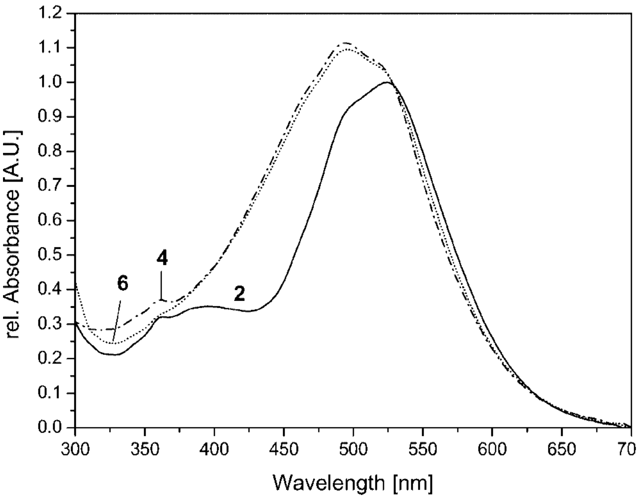


Figure 2. Solid-state UV/Vis spectra of thin films of the bis(perylenyl)-oligothiophenes **2**, **4**, and **6** spin-coated on glass (normalized to the maximum of the perylene absorption band).

With respect to potential applications in solar cells, of particular interest is the absorption behavior of the longer members **4** and **6** in the series which covers a broad range of the visible spectrum between 300 and 650 nm with high optical densities.

Corrected emission spectra for the whole series of compounds were measured in chloroform (Table 1). While $PDCI_2$ exhibits an intense and broad fluorescence with a maximum emission at 598 nm and a quantum yield of Φ = 81%, dimeric bis(perylenyl)-oligothiophenes **2**, **4**, and **6** exhibit weak, nonstructured broad emission bands. Almost irrespective of the oligothiophene chain length the fluorescence quantum yields are extremely small with values of 2% for quaterthiophene **2** and around 1% for the higher homologues **4** and **6**. In analogy to the linear perylenyl-oligothiophenes[5] where the same effect is observed, the strong fluorescence quenching can be attributed to a photoinduced-electron transfer from the donor system to the perylene acceptor.[12]

Electrochemical Properties

Oxidation and reduction potentials of the bis(perylenyl)-oligothiophenes **2**, **4**, and **6** were measured by cyclic voltammetry (CV) in dichloromethane using tetrabutylammonium hexafluorophosphate as the supporting salt and are referenced to the internal standard ferrocene/ferricenium (Fc/Fc^+) (Figure 3). To facilitate the assignment of the individual redox waves, $PDCI_2$ and the parent nonfunctionalized HT-O3HTs[10] are utilized as references. The redox potentials and the electrochemically determined bandgaps, ΔE_{CV}, measured as the potential difference between the onset of the first oxidation and the first reduction wave, respectively, are given in Table 2.

The reference compound $PDCI_2$ exhibits three reversible reductions ($E^\circ_{red1(P)}$ = –1.46 V, $E^\circ_{red2(P)}$ = –1.95 V, $E^\circ_{red3(P)}$ = –2.12 V), as well as two reversible oxidation waves at $E^\circ_{ox1(P)}$ = 0.89 V and at $E^\circ_{ox2(P)}$ = 1.06 V, respectively. While the first reduction occurs simultaneously for both perylene subunits and two electrons are transferred, the CV clearly reveals a mutual influence of the perylene moieties in the case of the oxidation and the second reduction due to two separated single redox processes. The nature of the two-electron process of the first reduction is a consequence of the extended π-system. The two electrons can be transferred onto the perylene dimer $PDCI_2$ at the same time, because they reside mainly on the electron-withdrawing imide oxygen atoms at both ends of the molecule. Therefore, the

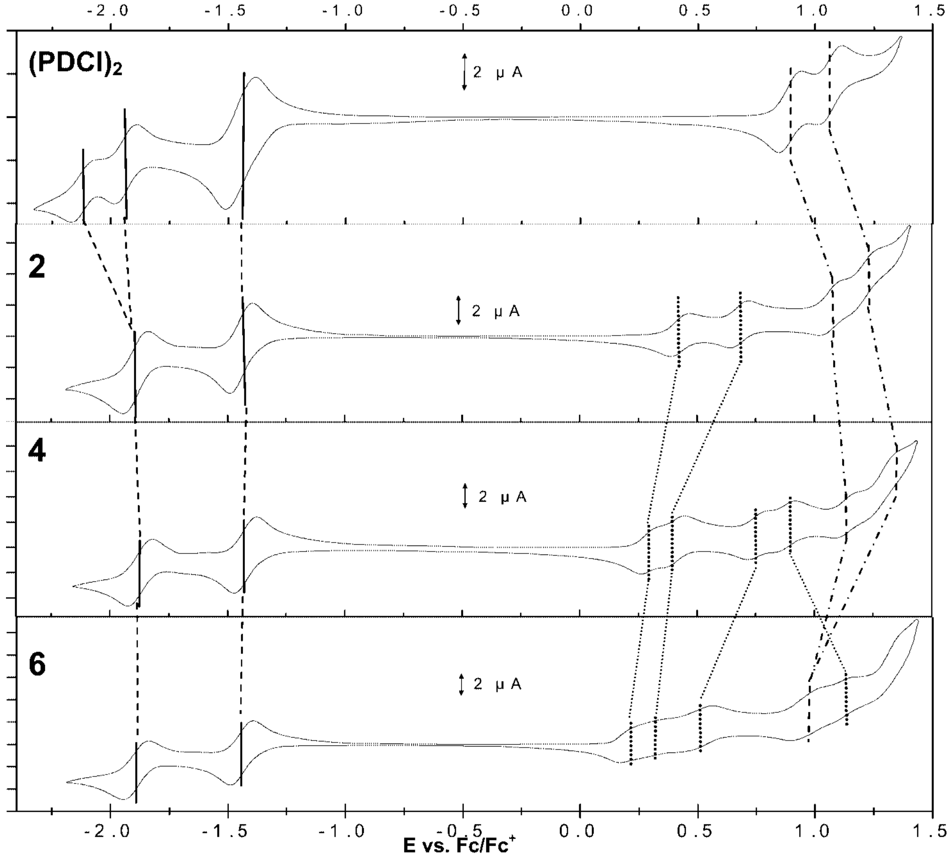


Figure 3. Electrochemical characterization of the bis(perylenyl)-oligothiophenes **2**, **4**, and **6** in dichloromethane/TBAHFP (0.1 M), scan speed 100 mV/s, potentials vs. Fc/Fc^+.

Table 2. Electrochemical properties of the bis(perylenyl)-oligothiophenes **2**, **4**, **6** and $PDCI_2$.

Compound	$E^\circ_{red2(P)}$[a] [V]	$E^\circ_{red1(P)}$[a] [V]	$E^\circ_{ox1(P)}$[a] [V]	$E^\circ_{ox2(P)}$[a] [V]	$E^\circ_{ox1(OT)}$[a] [V]	$E^\circ_{ox2(OT)}$[a] [V]	$E^\circ_{ox3(OT)}$[a] [V]	$E^\circ_{ox4(OT)}$[a] [V]	ΔE_{CV}[b] [V]
$PDCI_2$	–1.95 –2.12[d]	–1.46[c]	0.89	1.06					2.11
2 (4T)	–1.89[c]	–1.44[c]	1.08	1.24	0.43 (*0.43*)[e]	0.68 (*0.85*)[e]			1.70
4 (8T)	–1.90[c]	–1.45[c]	1.13	1.28	0.29 (*0.25*)[f]	0.40 (*0.34*)[f]	0.74 (*0.79*)[f]	0.88 (*0.98*)[f]	1.57
6 (12T)	–1.90[c]	–1.45[c]	0.96[c]		0.24 (*0.19*)[g]	0.30 (*0.27*)[g]	0.50 (*0.60*)[g]	1.16 (*1.01*)[g]	1.51

[a] In dichloromethane/nBu_4NPF_6 (0.1 M) vs. Fc/Fc^+ at 100 mV/s. P denotes perylene subunit, OT denotes oligothiophene. [b] Determined by $\Delta E_{CV} = E'_{ox1} - E'_{red1}$ (E′ is the potential at which the redox process starts). [c] Two-electron process. [d] Third reduction potential. [e] For comparison in parentheses values for the parent nonfunctionalized tetrahexyl-quaterthiophene. [f] Octahexyl-octithiophene. [g] Dodecahexyl-dodecithiophene.[10]

distance between the two electrons is maximal and any Coulombic repulsion can be neglected. Similar results have been obtained for terrylene and quaterrylene bis(imides) in aprotic solvents, where the first reduction is also observed as a two-electron process, while in the case of the smaller perylene bis(imide) the first reduction process is split up into two separate one-electron transfers.[13] For the second reduction of dimer $PDCI_2$, the third electron will be transferred onto one of the perylene moieties, where it should be localized over the aromatic ring system rather than at the imide group. Consequently, Coulombic repulsion will occur when the fourth electron is added to the neighboring perylene subunit, impeding this reduction process and hence, allowing it to occur at a more negative potential. Similar to the second reduction, the radical cation which is formed with the first oxidation is delocalized over the complete aromatic system. The direct interaction with the second positive charge, being transferred onto the adjacent perylene system aggravates the corresponding oxidation process, which in turn is shifted to a more positive potential.

Bis(perylene)-oligothiophenes **2**, **4**, and **6** exhibit two reversible reductions at $E°_{red1(P)}$ = –1.45 V and at $E°_{red2(P)}$ = –1.90 V, respectively, which can be allocated to the formation of stable radical anions and dianions. The generation of these radical anions occurs simultaneously for the two terminal perylene subunits and is independent of the chain length of the inserted oligothiophene moieties. The high currents observed during the first and second reduction can be attributed to the two-electron process. However, in the positive regime two different single-electron perylene oxidation waves are evident, giving rise to a communication between the terminal perylene subunits through the oligothiophene donor. The first perylene oxidation of the bis(perylene)-oligothiophenes **2**, **4**, and **6** is aggravated with respect to pristine perylene monoimide [$E°_{ox1}$(PDCI) = 0.95 V],[5] due to the electron-withdrawing capabilities of the attached oligothiophene moieties which are oxidized prior to the corresponding perylene units. In the case of bis(perylene)-oligothiophene **2**, the donor moiety is oxidized to a stable dication prior to the first oxidation of the terminal perylene moieties. As a consequence, the electron-deficient dication withdraws electron density from the neighboring perylene subunits, which in turn also become less electron-rich. In this respect, the relatively short π-system of quaterthiophene **2**, bearing a radical dication has a weaker influence than the tetracation delocalized over the larger conjugated system in octithiophene **4** as the perylene oxidation of **4** ($E°_{ox1}$ = 1.13 V) is impeded over the oxidation of the perylene moiety in **2** ($E°_{ox1}$ = 1.08 V). However, this effect is reversed by going to the longest homologue **6** as the corresponding perylene oxidation is facilitated ($E°_{ox1}$ = 0.96 V). Accordingly, the trication, being delocalized over a dodecithiophene in **6** is less electron-withdrawing than the tetracationic octithiophene of **4**.

For the smaller bis(perylenyl)-oligothiophenes **2** and **4**, two separate perylene oxidations are observed as in the case of the $PDCI_2$ oxidation. This leads to the assumption that the first oxidized perylene unit is electronically coupled through the oligothiophene entity with the other perylene acceptor at the opposite end of the system. Accordingly, the oxidation process of the second perylene is significantly aggravated ($\Delta E°_{ox} > 150$ mV). However, in the case of bis(perylenyl)-dodecithiophene **6** the perylene oxidation is observed as a two-electron process, implying that the oligothiophene chain has become too long to mediate the mutual electronic influence between the terminal perylene units.

The oxidation potentials of the oligothiophene moieties of the hybrid molecules **2**, **4**, and **6** are in good agreement with those of the comparable nonfunctionalized HT-O3HTs,[10] giving rise to almost electronically decoupled donor–acceptor systems. However, the first and second oligothiophene oxidations in general are slightly shifted towards more positive potentials as a consequence of the negative inductive effect of the terminal perylene monoimides, by withdrawing electron density from the donor moieties to some extent.

With increasing length of the oligothiophene chain, the first oxidation potential of the donor moiety is gradually shifted to more negative potentials from $E°_{ox1}$ = 0.43 V in the case of quaterthiophene **2** to $E°_{ox1}$ = 0.24 V for bis(perylenyl)-dodecithiophene **6**. This progressive shift is accompanied by an increasing number of redox processes, from four in the case of **2** to a final number of six in the case of **6**.

The bandgaps ΔE_{CV} were determined from the CVs by taking the difference between the onset of the first oxidation and reduction process (Table 2). The bandgap gradually becomes smaller when going from the reference compound $PDCI_2$ (2.11 eV) to bis(perylenyl)-dodecithiophene **6** (1.51 eV) reflecting the decreasing oxidation potential of the oligothiophene subunit. While the optically determined bandgap (ΔE_{opt}) always represents the electronic properties of the perylene units, the electrochemically determined bandgap (ΔE_{CV}) reflects the difference between the onset of the oligothiophene oxidation and the perylene reduction. As a consequence of the large deviation between ΔE_{CV} and ΔE_{opt} an almost perfect electronically separated donor–acceptor system has to be assumed.

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.[14] In order to calculate the absolute energies of the HOMO and LUMO levels of the bis(perylenyl)-oligothiophenes **2**, **4**, and **6** with respect to the vacuum level, the redox data are standardized to the ferrocene/fericenium couple which has a calculated absolute energy of –4.8 eV.[15] The bandgap energies result from the energy difference between the HOMO and the LUMO level. It can be seen in the corresponding energy diagram (Figure 4) that the HOMO–LUMO bandgap decreases with increasing chain length of the oligothiophene unit, which is due to the

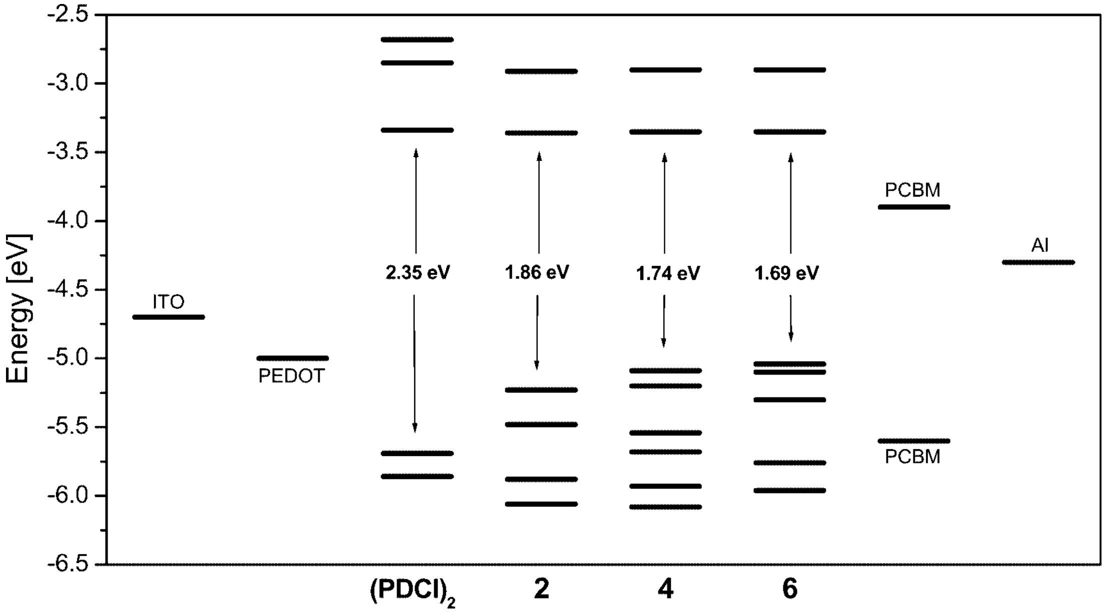


Figure 4. MO energy level diagram for the bis(perylenyl)-oligothiophenes **2**, **4**, and **6** and reference compound PDCI$_2$.

gradual decrease of the HOMO energy level with respect to a constant LUMO level. For comparison, bis(perylenyl)-oligothiophenes **2**, **4**, and **6** are related to the electrode work functions commonly used for the fabrication of standard photovoltaic devices. The work function of a poly(3,4-ethylenedioxythiophene)(PEDOT)-covered ITO electrode lies higher in energy terms with respect to the HOMOs of the donor–acceptor materials, allowing the holes to be easily injected from the cathode into the photoactive layer. On the other hand, the LUMOs of these hybrid systems are higher in energy with respect to both, the LUMO of fullerene derivative [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) and the work function of aluminum, making these hybrid systems suitable for the manufacture of single-layer or fullerene bulk-heterojunction photovoltaic devices.

In a standardized setup, a nonoptimized bulk-heterojunction device was manufactured, consisting of a PEDOT:PSS-covered ITO cathode, a 1:4 mixture of bis(perylenyl)-quaterthiophene **2**/PCBM as the photoactive layer and a top anode of aluminum. This device exhibited a photo response with an open-circuit voltage of V_{OC} = 0.68 V, a short-circuit current of I_{SC} = 0.7 mA/cm^2 and a fill factor of *FF* = 0.31, resulting in moderate power conversion efficiencies of 0.2% under calculated standard test conditions (AM, 1.5 G, 1000 W/m^2).

Conclusion

We synthesized a series of hybrid systems, consisting of head-to-tail-coupled oligo(3-hexylthiophene)s integrated between two terminal perylene monoimides. While the type of perylene acceptor remained unchanged, the oligothiophene donor system has been systematically varied in length from a tetramer to a dodecamer. These novel π-acceptor–π-donor–π-acceptor systems were obtained by an optimized palladium-catalyzed Ullmann-type reaction. 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, redox potentials and energy gaps. Clear structure-property relationships of the novel type of triad molecules provide a valuable data set for their application in organic solar cells. The fabrication and characterization of the corresponding photovoltaic devices based on a blend of bis(perylenyl)-quaterthiophene **2** with PCBM revealed a power conversion efficiency of 0.2% under a simulated terrestrial sun spectrum.

Experimental Section

General Procedures: ^{1}H NMR spectra were recorded in CDCl$_3$ with a Bruker AMX 400 at 400 MHz. ^{13}C NMR spectra were recorded in CDCl$_3$ with a Bruker AMX 400 at 100 MHz. Chemical shifts are denoted in δ units (ppm), and were referenced to internal tetramethylsilane (δ =0.0 ppm). The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet) and the assignments are Pery (perylene), Ph (phenyl), Th (thiophene) for ^{1}H NMR spectroscopy. 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 with 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 with a Varian CP-3800 gas chromatograph. HPCL analyses were performed with a Shimadsu SCL-10A equipped with an SPD-M10A photodiode array detector and an SC-10A solvent delivery system using a LiChrosphor column (Silica 60, 5 µm, Merck). Thin-layer chromatography was carried out with Silica Gel 60 F$_{254}$ aluminum plates (Merck). Developed plates were dried and examined under a UV lamp. Preparative column chromatography was carried out with glass columns of different sizes packed with silica gel Merck 60 (40–63 µm). UV/Vis spectra were recorded with a Perkin–Elmer Lambda 19 in 1-cm cuvettes. Thin uniform films for solid-state spectra were obtained with a POLOS wafer spinner from a toluene solution (20 mg/ml) 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) (Φ = 0.9 in chloroform[16]). 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 potentials were internally referenced to the ferrocene/ferricenium couple.[15] For the measurements concentrations of 10^{-3} mol/L of the electroactive species were used in freshly distilled and deaerated dichloromethane (Lichrosolv, Merck) and 0.1 м 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 the usual methods prior to use and typically used under inert gas. The following starting materials were purchased and used without further purification: Palladium(II) acetate (Merck) and tri(*tert*-butyl)phosphane (Acros). PDCI$_2$ was synthesized according to a literature procedure.[11]

General Procedure for the Dimerization of Iodinated Perylenyl-Oligothiophenes: The iodinated perylenyl-oligothiophene (1 equiv.), hydroquinone (0.5 equiv.) and cesium carbonate (1 equiv.) were dissolved in dry dimethylacetamide (DMA). Next, palladium acetate (5–10 mol-%) and tri(*tert*-butyl)phosphane (5–10 mol-%) as a 0.01 м solution in DMA were added. The resulting solution was carefully degassed and stirred at 80 °C for 24 h. Next, the crude product was precipitated by adding water and filtered off. The black solid was purified by column chromatography.

8,8′-(3′,4,4′′,4′′′-Tetrahexyl-2,2′:5′,2′′:5′′,2′′′-quaterthiene-5,5′′′-diyl)bis[2-(2,6-diisopropylphenyl)-1*H*-benzo[5,10]anthra[2,1,9-*def*]isoquinoline-1,3(2*H*)-dione] (2): According to the general procedure, to a solution of **1** (120 mg, 0.13 mmol), hydroquinone (7 mg, 65 µmol), and cesium carbonate (42 mg, 0.13 mmol) in DMA (2.5 mL) were added palladium acetate (0.65 mL of a 0.01 м solution, 5 mol-%) and tri(*tert*-butyl)phosphane (5 mol-%) in DMA. The reaction was carried out at 80 °C for 24 h to give **2** (80 mg, 76%) as a black solid after column chromatography [dichloromethane/petroleum ether (2:1)]. M.p. 218–219 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.67 (d, *J* = 8.0 Hz, 4 H, Pery-1-*H*, 6-*H*, 1′-*H*, 6′-*H*), 8.55–8.41 (m, 8 H, Pery-2-*H*, 5-*H*, 7-*H*, 12-*H*, 2′-*H*, 5′-*H*, 7′-*H*, 12′-*H*), 8.02 (d, *J* = 8.5 Hz, 2 H, Pery-8-*H*, 8′-*H*), 7.71 (d, *J* = 7.7 Hz, 2 H, Pery-10-*H*, 10′-*H*), 7.66 (t, *J* = 7.8 Hz, 2 H, Pery-11-*H*, 11′-*H*), 7.50 (t, *J* = 7.8 Hz, 2 H, Ph-4-*H*, 4′-*H*), 7.37 (d, *J* = 7.8 Hz, 4 H, Ph-3-*H*, 5-*H*, 3′-*H*, 5′-*H*), 7.18 (s, 2 H, Th-3-*H*, Th′′′-3-*H*), 7.09 (s, 2 H, Th′-4-*H*, Th′′-3-*H*), 2.90–2.75 [m, 8 H, Ph-C*H*(CH$_3$)$_2$, Th-α′-C*H*$_2$, α′′-C*H*$_2$], 2.48 (t, *J* = 7.5 Hz, 4 H, Th-α-C*H*$_2$, α′′′-C*H*$_2$), 1.82–1.70 (m, 4 H, Th-β′-C*H*$_2$, β′′-C*H*$_2$), 1.65–1.55 (m, 4 H, Th-β-C*H*$_2$, β′′′-C*H*$_2$), 1.50–1.40 (m, 4 H, Th-γ′-C*H*$_2$, γ′′-C*H*$_2$), 1.40–1.10 (m, 20 H, C*H*$_2$), 1.21 [d, *J* = 6.8 Hz, 24 H, Ph-CH(C*H*$_3$)$_2$], 0.87–0.83 (m, 6 H, Th′-C*H*$_3$, Th′′-C*H*$_3$), 0.80 (t, *J* = 7.1 Hz, 6 H, Th-C*H*$_3$, Th′′′-C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 162.94, 144.72, 141.01, 139.42, 136.50, 136.22, 134.88, 133.83, 133.07, 132.88, 131.01, 130.05, 129.49, 129.37, 128.65, 128.41, 127.26, 126.31, 126.24, 125.88, 125.63, 123.01, 122.08, 120.14, 120.07, 119.40, 119.32, 30.68, 30.48, 29.51, 29.44, 28.62, 28.26, 28.17, 28.03, 27.91, 23.01, 21.61, 21.59, 21.47, 13.08, 12.98 ppm. MS (MALDI-TOF): *m*/*z* (%) = 1625 [M + H]$^+$. C$_{108}$H$_{108}$N$_2$O$_4$S$_4$ (1626.30): calcd. C 78.30, H 7.12, N 1.52; found C 78.40, H 7.05, N 1.60.

8,8′-(4,3′,3′′,3′′′,4′′′′,4′′′′′,4′′′′′′,4′′′′′′′-Octahexyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′:5′′′′′,2′′′′′′:5′′′′′′,2′′′′′′′-octithiene-5,5′′′′′′′-diyl)bis[2-(2,6-diisopropylphenyl)-1*H*-benzo[5,10]anthra[2,1,9-*def*]isoquinoline-1,3(2*H*)-dione] (4): According to the general procedure, to a solution of **3** (127 mg, 0.1 mmol), hydroquinone (6 mg, 50 µmol), cesium carbonate (33 mg, 0.1 mmol) in DMA (1 mL) were added palladium acetate (1 mL of a 0.01 м solution, 10 mol-%) and tri(*tert*-butyl)phosphane (10 mol-%) in DMA. The reaction was carried out at 80 °C for 24 h to give **4** (90 mg, 79%) as a black solid after column chromatography [dichloromethane/petroleum ether (2:1)]. M.p. 163–164 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.67 (d, *J* = 7.5 Hz, 4 H, Pery-1-*H*, 6-*H*, 1′-*H*, 6′-*H*), 8.52–8.41 (m, 8 H, Pery-2-*H*, 5-*H*, 7-*H*, 12-*H*, 2′-*H*, 5′-*H*, 7′-*H*, 12′-*H*), 8.01 (d, *J* = 8.3 Hz, 2 H, Pery-8-*H*, 8′-*H*), 7.69 (d, *J* = 7.6 Hz, 2 H, Pery-10-*H*, 10′-*H*), 7.64 (t, *J* = 7.5 Hz, 2 H, Pery-11-*H*, 11′-*H*), 7.48 (t, *J* = 7.8 Hz, 2 H, Ph-4-*H*, 4′-*H*), 7.35 (d, *J* = 7.7 Hz, 4 H, Ph-3-*H*, 5-*H*, 3′-*H*, 5′-*H*), 7.17 (s, 2 H, Th-3-*H*, Th′′′′′′′-3-*H*), 7.10–6.90 (m, 6 H, Th-4′-*H*, 4′′-*H*, 4′′′-*H*, 3′′′′-*H*, 3′′′′′-*H*, 3′′′′′′-*H*), 2.90–2.74 [m, 16 H, Ph-C*H*(CH$_3$)$_2$, Th-α′-C*H*$_2$, α′′-C*H*$_2$, α′′′-C*H*$_2$, α′′′′-C*H*$_2$, α′′′′′-C*H*$_2$, α′′′′′′-C*H*$_2$], 2.46 (t, *J* = 7.3 Hz, 4 H, Th-α-C*H*$_2$, α′′′′′′′-C*H*$_2$), 1.80–1.50 (m, 16 H, C*H*$_2$), 1.50–1.30 (m, 32 H, C*H*$_2$), 1.30–1.05 (m, 16 H, C*H*$_2$), 1.20 [d, *J* = 6.8 Hz, 24 H, Ph-CH(C*H*$_3$)$_2$], 0.95–0.80 (m, 18 H, Th′-C*H*$_3$, Th′′-C*H*$_3$, Th′′′-C*H*$_3$, Th′′′′-C*H*$_3$, Th′′′′′-C*H*$_3$, Th′′′′′′-C*H*$_3$), 0.78 (t, *J* = 6.7 Hz, 6 H, Th-C*H*$_3$, Th′′′′′′′-C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 163.56, 145.64, 141.90, 139.87, 137.43, 137.17, 134.83, 133.81, 133.74, 131.95, 130.97, 130.41, 130.28, 129.35, 128.56, 128.18, 127.22, 127.15, 126.81, 123.92, 123.01, 121.04, 120.98, 120.32, 120.23, 31.60, 31.39, 30.48, 30.37, 30.34, 29.47, 29.43, 29.21, 29.17, 29.08, 29.02, 28.94, 28.83, 23.93, 22.54, 22.39, 14.02, 14.00, 13.89 ppm. MS (MALDI-TOF): *m*/*z* (%) = 2290 [M + H]$^+$. C$_{148}$H$_{164}$N$_2$O$_4$S$_8$ (2291.42): calcd. C 77.58, H 7.21, N 1.22; found C 77.51, H 7.13, N 1.18.

8,8′-(4,3′,3′′,3′′′,3′′′′,3′′′′′,4′′′′′′,4′′′′′′′,4′′′′′′′′,4′′′′′′′′′,4′′′′′′′′′′,4′′′′′′′′′′′-Dodecahexyl-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′:5′′′′′,2′′′′′′:5′′′′′′,2′′′′′′′:5′′′′′′′,2′′′′′′′′:5′′′′′′′′,2′′′′′′′′′:5′′′′′′′′′,2′′′′′′′′′′:5′′′′′′′′′′,2′′′′′′′′′′′dodecithiene-5,5′′′′′′′′′′′-diyl)bis[2-(2,6-diisopropylphenyl)-1*H*-benzo[5,10]anthra[2,1,9-*def*]isoquinoline-1,3(2*H*)-dione] (6): According to the general procedure, to a solution of **5** (40 mg, 25 µmol), hydroquinone (2 mg, 13 µmol), cesium carbonate (9 mg, 25 µmol) in DMA (0.25 mL) were added palladium acetate (0.25 mL of a 0.01 м solution, 10 mol-%) and tri(*tert*-butyl)phosphane (10 mol-%) in DMA. The reaction was carried out at 60 °C for 24 h to give **6** (25 mg, 68%) as a black solid after column chromatography [dichloromethane/petroleum ether (2:1)]. M.p. 141–142 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.68 (d, *J* = 8.0 Hz, 4 H, Pery-1-*H*, 6-*H*, 1′-*H*, 6′-*H*), 8.55–8.45 (m, 8 H Pery-2-*H*, 5-*H*, 7-*H*, 12-*H*, 2′-*H*, 5′-*H*, 7′-*H*, 12′-*H*), 8.01 (d, *J* = 8.5 Hz, 2 H, Pery-8-*H*, 8′-*H*), 7.71 (d, *J* = 7.8 Hz, 2 H, Pery-10-*H*, 10′-*H*), 7.66 (t, *J* = 7.9 Hz, 2 H, Pery-11-*H*, 11′-*H*), 7.49 (t, *J* = 7.8 Hz, 2 H, Ph-4-*H*, 4′-*H*), 7.35 (d, *J* = 7.7 Hz, 4 H, Ph-3-*H*, 5-*H*, 3′-*H*, 5′-*H*), 7.17 (s, 2 H, Th-3-*H*, Th′′′′′′′′′′′-3-*H*), 7.05–6.95 (m, 10 H, Th-4′-*H*, 4′′-*H*, 4′′′-*H*, 4′′′′-*H*, 4′′′′′-*H*, 4′′′′′′-*H*, 3′′′′′′′-*H*, 3′′′′′′′′-*H*, 3′′′′′′′′′-*H*, 3′′′′′′′′′′-*H*), 2.90–2.75 [m, 24 H, Ph-C*H*(CH$_3$)$_2$, Th-α′-C*H*$_2$, α′′-C*H*$_2$, α′′′-C*H*$_2$, α′′′′-C*H*$_2$, α′′′′′-C*H*$_2$, α′′′′′′-C*H*$_2$, α′′′′′′′-C*H*$_2$, α′′′′′′′′-C*H*$_2$, α′′′′′′′′′-C*H*$_2$, α′′′′′′′′′′-C*H*$_2$], 2.46 (t, *J* = 7.4 Hz, 4 H, Th-α-C*H*$_2$, α′′′′′′′′′′′-C*H*$_2$), 1.80–1.51 (m, 24 H, C*H*$_2$), 1.51–1.41 (m, 24 H, C*H*$_2$), 1.41–1.10 (m, 48 H, C*H*$_2$), 1.20 [d, *J* = 6.8 Hz, 24 H, Ph-CH(C*H*$_3$)$_2$], 0.97–0.80 (m, 30 H, Th′-C*H*$_3$, Th′′-C*H*$_3$, Th′′′-C*H*$_3$,

$\mathrm{Th}''''\text{-}\mathrm{C}H_3$, $\mathrm{Th}'''''\text{-}\mathrm{C}H_3$, $\mathrm{Th}''''''\text{-}\mathrm{C}H_3$, $\mathrm{Th}'''''''\text{-}\mathrm{C}H_3$, $\mathrm{Th}''''''''\text{-}\mathrm{C}H_3$, $\mathrm{Th}'''''''''\text{-}\mathrm{C}H_3$, $\mathrm{Th}''''''''''\text{-}\mathrm{C}H_3$), 0.78 (t, J = 6.7 Hz, 6 H, $\mathrm{Th}\text{-}\mathrm{C}H_3$, $\mathrm{Th}'''''''''''\text{-}\mathrm{C}H_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.87, 145.61, 141.89, 140.26, 139.86, 139.84, 137.49, 137.23, 135.75, 134.84, 134.57, 133.91, 133.81, 133.74, 133.61, 132.01, 130.92, 130.44, 130.30, 129.45, 129.33, 129.30, 128.52, 128.18, 127.24, 127.10, 126.83, 126.49, 123.99, 123.93, 123.06, 121.01, 120.95, 120.35, 120.26, 31.62, 31.40, 30.50, 30.40, 30.34, 29.39, 29.18, 29.05, 28.93, 28.83, 23.94, 22.57, 22.56, 22.53, 22.41, 14.05, 14.03, 13.93 ppm. MS (MALDI-TOF): m/z (%) = 2955 [M + H]$^+$. $C_{188}H_{220}N_2O_4S_{12}$ (2956.55): calcd. C 76.37, H 7.50, N 0.95; found C 76.24, H 7.42, N 0.88.

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