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Synthesis of Conjugated Fluorene-*alt*-thiophene Polymers with Pendant Perylenediimide Units

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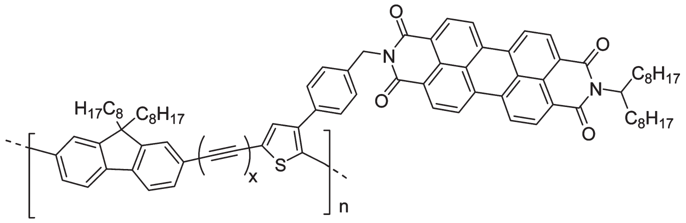

X= 0, **PDI-PFT**
X= 1, **PDI-PFET**

In this article we present the synthesis, characterization, electrochemical, optical, and preliminary photophysical investigation of two novel poly(fluorene-*alt*-thiophene) conjugated polymers endowed with pendant perylenediimide electron acceptor units. We show a route to the synthesis of easily functionalizable monomers paving the way to the preparation of a variety of functionalized polymers with different properties and applications and reflecting the versatility of this synthetic methodology.

Introduction

The exploration of organic semiconductors as active elements in electronic devices, such as light emitting diodes,[1] thin film transistors,[2] solid-state lasers,[3] or organic solar cells,[4] has experienced much progress in recent years. This progress has been possible due to the unique features that organic semiconductors offer, such as the tuning of the electronic properties, easy structural modifications, possibility of self-assembly, or mechanical flexibility. All this enables the exploitation of organic semiconductors as materials for large-area and low-cost disposable electronic products.

Photoinduced electron transfer has a great importance in both life and science. It is the fundamental process on which photosynthesis is based and it also constitutes the basis of molecular electronics.[4] In this respect, the unique features that organic semiconductors offer, e.g. the tuning of absorption and emission properties, REDOX behavior, or HOMO–LUMO band gaps by easy structural modifications, have prompted the synthesis of a variety of molecular architectures combining electron donor fragments covalently linked to acceptor units and exhibiting the transfer of one electron from the donor to the acceptor unit after photoexcitation.[5]

The backbones of conjugated polymers can be covalently linked to functional groups which provide specific physical and chemical properties. In recent years this approach has been widely explored and proved to be appealing in order to obtain materials with novel properties and applications, such as sensors[6] or electrochromic or energy conversion materials.[4] In the latter regard, electron donor polymers substituted with electron acceptor groups have been proposed as promising candidates.[7] Thus, in our pursuit of functional donor–acceptor polymers, we have used different pendant electron acceptor

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groups such as fullerenes,[8] anthraquinones,[9] or tetracyanoanthraquinodimethane.[10]

Perylenediimide (PDI) derivatives have evolved into one of the most fascinating materials in both industry and academics due to its good chemical stability, thermal stability, and photostability.[11] Specially remarkable for the construction of systems showing photoinduced electron transfer are its good electron accepting ability and high absorption of light in the visible. Thus PDIs have been attached to [60]fullerene,[12] oligophenylenevinylenes,[13] pyrenes,[14] oligothiophenes,[15] phthalocyanines,[16] porphirins,[17] or tetrathiafulvalene (TTF).[18] PDI has also been introduced in the main chain of polymers[19] and, interestingly, covalently attached as pendant groups to conjugated polymers. Our research group has been especially active within this particular field.[20] Thus, we have shown interesting photophysical processes in this type of materials,[20a,c,d] aggregation phenomena via the $\pi-\pi$ stacking of the pendant perylenediimide units,[21] or the variation of the bandgap.[20b]

In this article we go a step further in our investigation of this type of materials and we present the synthesis, characterization, electrochemical, optical, and preliminary photophysical investigation of two novel poly(fluorene-*alt*-thiophene) conjugated polymers endowed with pendant perylenediimide electron acceptor units. Furthermore we show a route to the synthesis of easily functionalizable monomers paving the way to the preparation of a variety of functionalized polymers with different properties and applications and reflecting the versatility of this synthetic methodology.

Results and Discussion

Synthesis. The preparation of the donor−acceptor poly(fluorene-*alt*-thiophene)s bearing PDI units **PDI-PFT** and **PDI-PFET** (Scheme 3) and their respective reference polymers, i.e. the same polymeric main chain without the pendant perylenediimide units, namely poly[2,7-(9,9-dioctylfluorene)-*alt*-2,5-thiophene] (**PFT**)[22] and poly(9,9-dioctylfluoren-2,7-yleneethylene-*alt*-2,5-thiophene) (**PFET**) (Scheme 3), has been carried out by using classical palladium-catalyzed coupling reactions between a 2,5-dibromothiophene derivative bearing a perylenediimide moiety and appropriately 2,7-difunctionalized fluorene monomers. This approach has the advantage to yield structurally well-defined alternating copolymers, thus allowing control over the polymer structure to be gained and making possible the tuning of the gradient of redox potentials and their optical band gap, which are important factors that determine the photophysical behavior of these materials, by suppressing the spacer or introducing a triple bond.

Synthesis of the 2,5-Dibromothiophene-perylenediimide Monomer. The synthesis of the key monomer 2,5-dibromothiophene-perylenediimide (**10**) (Scheme 2), used in the synthesis of both perylenediimide functionalized polymers **PDI-PFT** and **PDI-PFET**, has been accomplished following two alternative approaches, involving either the 2,5-dibromothiophene derivatives **5** or **7**, whose synthesis is depicted in Scheme 1. Besides, many of the prepared intermediates are also interesting building blocks for the preparation of other functional monomers and polymers following an analogous synthetic route, as we have mentioned.

As the direct bromination of thiophenes with molecular bromine usually gives a mixture of mono- and dibromothiophenes, which cannot always be easily separated, better results can be attained with *N*-bromosuccinimide (NBS) as the brominating agent. Indeed, bromination of arenes with NBS is known to proceed with especially high selectivity in dipolar-aprotic solvents, e.g. *N*,*N*-dimethylformamide (DMF).[23] Thus, regioselective dibromination of 4′-thien-3-ylbenzonitrile (**1**)[24] in the thiophene α-positions with 2 mol equiv readily affords in a smooth reaction the corresponding 2,5-dibromo-3-(4′-cyanophenyl)thiophene (**2**) in excellent yield (Scheme 1). Subsequent diisobutyl aluminum hydride (DIBAL-H) reduction of the cyano group in **2** to aldehyde provides **3** in 93% yield. Compound **3** is a common precursor to the two approaches followed toward 2,5-dibromothiophene-perylenediimide monomer (**10**) (Scheme 2). The first synthetic approach investigated involves the preparation of the thiophene derivative **5**.[25] This synthon is functionalized with three bromine atoms: one in a lateral chain, which is suitable for nucleophilic substitution (e.g. with a complementarily functionalized perylenediimide derivative),

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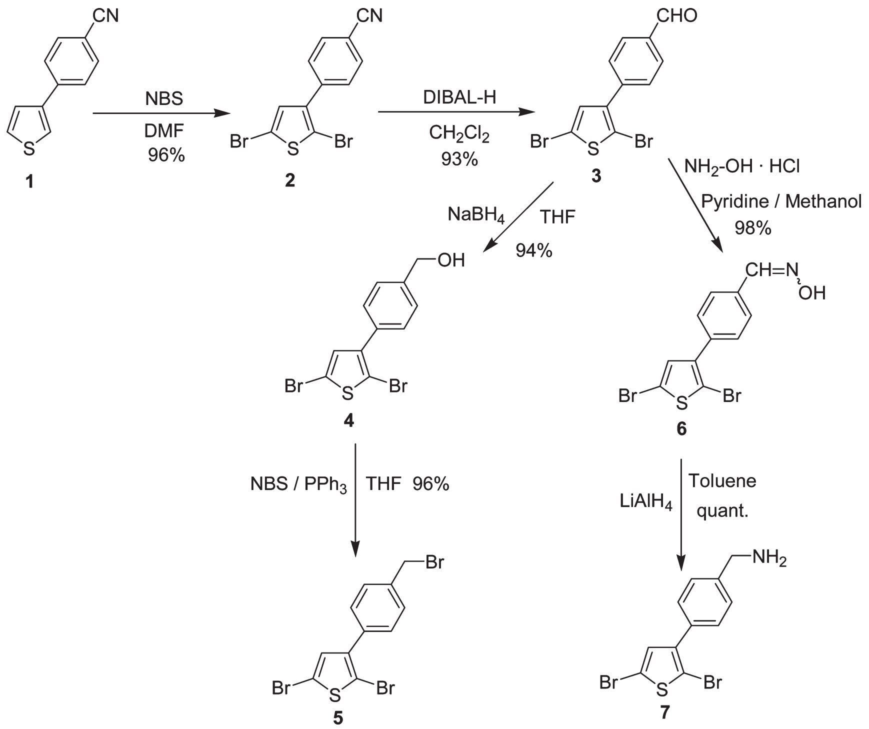
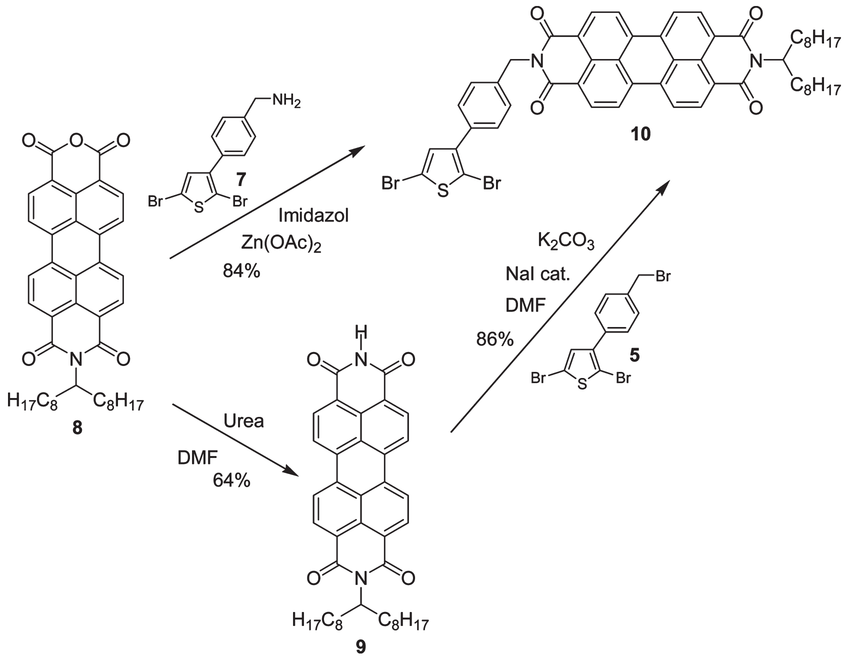
SCHEME 1



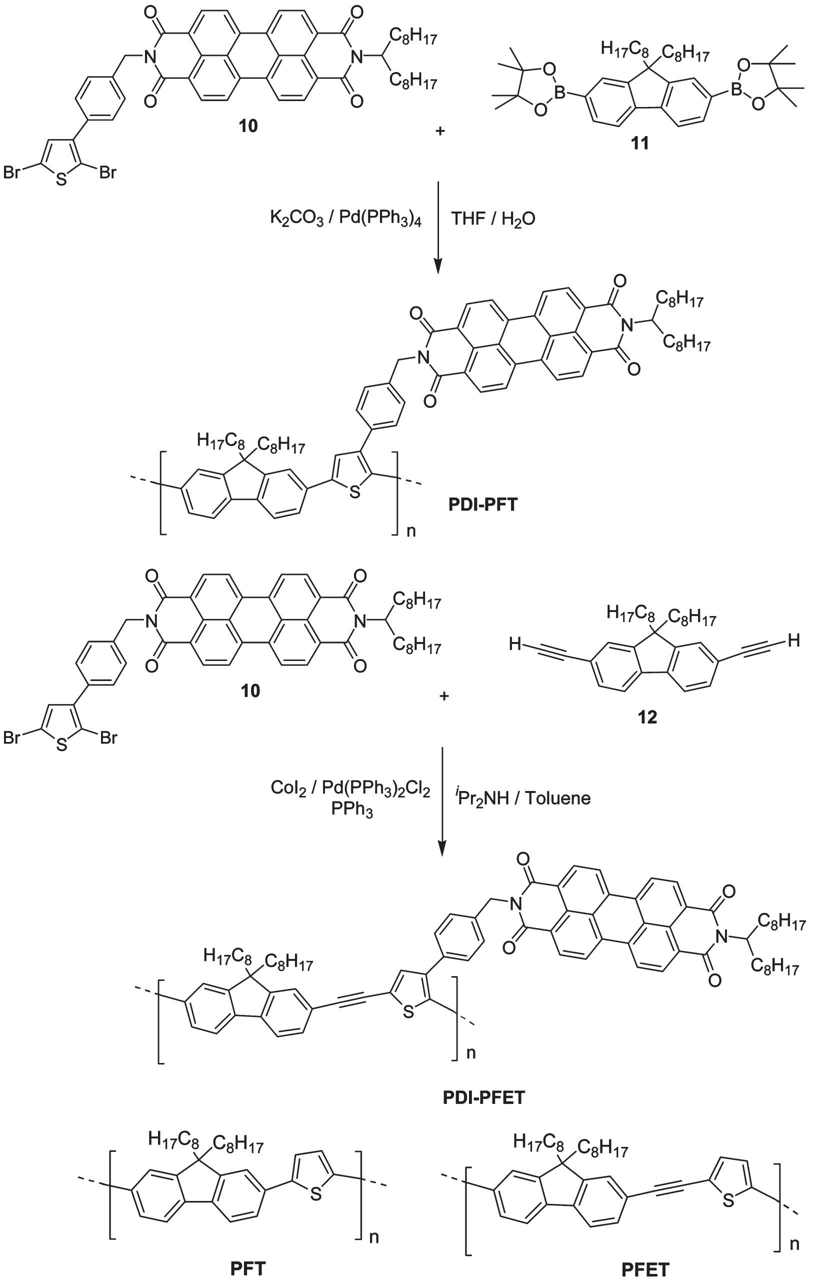
SCHEME 2



whereas the other two have been covalently attached to the α-positions of the thiophene core, and thus are suitable for palladium-catalized couplings, for instance with fluorene monomers functionalized with either a boronic ester (**11**) (Suzuki coupling) or terminal acetylene groups (**12**) (Sonogashira reaction). Thus, sodium borohydride reduction of aldehyde **3** readily affords hydroxymethyl derivative **4**, which can be easily halogenated to yield the target bromomethyl derivative **5**. Following our methodology, this interesting precursor for the preparation of chemically polymerizable functionalized monomers has been obtained in 82% overall yield after four steps, much higher than with the previously reported synthetic protocol (five steps, 25% yield).[25]

On the second synthetic approach, the treatment of aldehyde **3** with an excess of hydroxylamine hydrochloride in methanol, in the presence of a catalytic amount of pyridine, affords in nearly quantitative yield the corresponding oxyme **6**, which can be subsequently reduced with lithium aluminum hydride to the

SCHEME 3



corresponding amino-functionalized thiophene derivative 2,5-dibromo-3-[4′-(aminomethyl)phenyl]thiophene (**7**). It is worth noting that, in our hands, the direct hydride reduction of the cyano derivative **2** to the corresponding amine **7** gives a complex mixture of compounds, out of which no **7** could be isolated. Finally, **7** can be directly used to condense it in good yield with the corresponding *N*-(9-octylnonyl)perylene-3,4:9,10-tetracarboxylic acid monoimide monoanhydride (**8**)[26] by the classical protocol followed for the attachment of perylenediimides to a variety of systems, i.e. direct heating in toluene for 24 h in the presence of zinc acetate (Scheme 2).

The alternative synthetic approach also shown in Scheme 2 toward the 2,5-dibromothiophene-perylenediimide monomer **10** is based on the alkylation of imides. This procedure, although certainly much less exploited in perylenediimide chemistry than the former, is of high value as it constitutes a good alternative for the preparation of unsymmetrically substituted perylenediimides from difficult to prepare or unstable amines. Thus, the presence in **9**, readily affordable from the parent monoimide monoanhydride **8** by heating with urea, of an acidic imido hydrogen enables its further and convenient functionalization by an *N*-alkylation reaction with the complementary functionalized 2,5-dibromo-3-[4′-(bromomethyl)phenyl]thiophene (**5**), using potassium carbonate as the base and sodium iodide as catalyst. The presence in the perylenediimide moiety of long and branched alkyl chains endowes monomer **10** with good solubility in common organic solvents. Both synthetic sequences leading to 2,5-dibromothiophene-perylenediimide (**10**) monomer, shown in Scheme 2, provide analytically

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identical batches of product in good yield. Thus, the ^{1}H NMR spectrum of monomer **10** displays at low fields a series of duplets and multiplets arising from the unsymmetrical perylenediimide aromatic core. Besides, the AA′BB′ system of the benzene spacer is clearly shown around 7.5 ppm, and the singlet corresponding to the 3-thiophene position appears at 6.9 ppm. The ^{1}H NMR spectrum is finally completed with a singlet (integrating two protons) corresponding to the methylene group linked to the benzene and the imide nitrogen, a multiplet (one proton) arising from the methyne group directly linked to the imide nitrogen, and the signals corresponding to the swallow-tail solubilizing chains. In the ^{13}C NMR spectrum the carbonyl imide groups of the PDI moiety are clearly visible at around 163 ppm together with the signals of the aromatic carbons in the sp^2 region, the methylene and methyne groups linked to the nitrogen (55 ppm), and the signals of the alkyl chain. As the PDI moiety in **10** is not fully symmetrical, one could expect four carbonyl signals in its ^{13}C NMR spectrum, in spite of the free rotation around the C−N bond. However, our spectrum shows only two carbonyl signals: one sharp and another weak, which is the characteristic pattern of the nonsymmetrical perylenediimides reported in this article and also has been established in the literature.[27] Actually, the doubling of carbonyl signals from swallowtailed imides suggests that the swallowtails assume an asymmetrical conformation. The FTIR spectra of monomer **10** show the characteristic absorption pattern of the perylene skeleton with bands at 1580 and 1595 cm^{-1}. Besides, the absorption bands at 1658 and 1698 cm^{-1} indicate the presence of the imide group. Finally, further evidence concerning the structure proposed for monomer **10** is given by mass spectrometry and evidence concerning its purity by elemental analyses, which reveal mass percentages that are in accordance with the expected values.

Synthesis of Electron Donor−Acceptor Polymers PDI-PFT and PDI-PFET. Polymer **PDI-PFT** (Scheme 3) has been synthesized by a Suzuki polycondensation of an equimolecular mixture of the perylenediimide functionalized 2,5-dibromothiophene monomer **10** and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**11**)[28] in the presence of 5 mol % Pd(PPh$_3$)$_4$ in a mixture of dry degassed THF and aqueous potassium carbonate for 72 h under reflux (Scheme 3). Although boronic acids have been often directly used as reagents in poly-Suzuki couplings, boronic esters like **11** have proven to be more advantageous in this kind of reaction, since the presence of the 1,1,2,2-tetramethylethylene glycol units has a protective effect on the labile boronic acid precursor. Simultaneously to the polymerization, a hydroxylation deprotection process takes place, in which the removal of such protecting groups as ethylene glycol does not affect the couplings.[29]

On the other hand, the copolymer **PDI-PFET** (Scheme 3) was synthesized by a Sonogashira polycondensation of an equimolecular mixture of the perylenediimide functionalized 2,5-dibromothiophene monomer **10** and 2,7-diethynyl-9,9-dioctylfluorene (**12**)[30] in the presence of a palladium(II) catalyst and triphenylphosphine (Scheme 1). The experimental conditions require the use of an amine as base (^{i}Pr$_2$NH) and a copper(I) salt (CoI) as a cocatalyst, whose role is probably to activate the alkyne toward the transmetalation step by forming copper σ- or π-acetylides. The formation of butadiyne defects is one of the major drawbacks of the polymerization coupling between bis(ethynyl) aromatic derivatives and dihaloarenes to yield poly(arylene ethynylene)s (PAEs). When Pd (II) is used, such defects are originated partly by the reduction of Pd(II) to Pd(0) in the catalyst activation step, but defects also derive from the oxidative coupling of terminal bonds; the source of the oxidizing agent remains unclear and cannot be avoided even under strict exclusion of air.[31] Even the use of Pd(0) complexes does not eliminate the occurrence of butadyine units in the polymeric chain. Although there is no direct measure to determine the amount of butadiyne defects in PAEs, with an estimated number ranging from 1% to 10% of all repeating units,[32] ^{13}C NMR can be useful sometimes. In our case no signals could be assigned to diyne defects showing that the number of diyne defects is below the detection limit, that the noise of the spectra hinders those signals to some extent, or, taking into account the complexity of our spectra, those signals could be overlapped. However, it is generally accepted that butadiyne defects do not have a remarkable effect on either the optical or the electronic properties of the PAEs.

The resulting copolymers **PDI-PFT** and **PDI-PFET** were precipitated out of their respective thick reaction mixtures by addition of methanol, purified by reprecipitation from chloroform/methanol and further purified by washing with acetone in a Soxhlet apparatus for 24 h to remove unreacted materials, small molecules, oligomers, and catalyst residues. The contamination by palladium nanoparticles formed during the palladium-catalyzed chemical reaction is an important drawback of these protocols. Metallic residues can act as charge-trapping sites, thus impairing the charge carrier mobility and/or producing device hysteresis.[33] A few methods have been developed to remove such nanoparticles although they tend to be relatively harsh or not generally applicable.[34] Happily, a substantial part of this palladium contamination can be easily removed by a simple Soxhlet extraction, as in our purification protocol.

To be used as reference materials we have also synthesized poly[2,7-(9,9-dioctylfluorene)-*alt*-2,5-thiophene] (**PFT**)[22] and poly(9,9-dioctylfluoren-2,7-yleneethylene-*alt*-2,5-thiophene) (**PFET**) by analogous Suzuki or Sonogashira couplings between 2,5-dibromothiophene and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**11**) or 2,7-diethynyl-9,9-dioctylfluorene (**12**) under the same conditions as previously described for functionalized copolymers **PDI-PFT** and **PDI-PFET**. Following the same experimental procedure, reference polymers were precipitated out of the reaction mixtures by addition of methanol, purified by reprecipitation from chloroform/methanol and further purified by washing with acetone in a Soxhlet apparatus.

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TABLE 1. **Electrochemical Data[a] and SEC Characterization of Donor−Acceptor Copolymers PDI-PFT and PDI-PFET and Their Respective Reference Copolymers PFT and PFET and Dialkyl-PDI**

compd	$E^1{}_{1/2\mathrm{red}}$	$E^2{}_{1/2\mathrm{red}}$	$E^1{}_{\mathrm{ox}}$	$E^2{}_{\mathrm{ox}}$	M_n	M_w	pd
PDI-PFET	−1.12	−1.31	0.33	1.29	30 300	5 800	5.2
PDI-PFT	−1.12	−1.30	0.38		46 900	10 200	4.6
PFET			0.35	1.30	75 900	26 200	2.9
PFT			0.36		98 200	57 800	1.7
Dialkyl-PDI	−1.11	−1.31					

[a] In dichloromethane solutions, using platinum as working and counter electrode and tetrabutylammonium hexafluorophosphate (10^{-3} M) as supporting electrolyte. Room temperature; scan rate: 200 mV/s. Values vs. Fc/Fc$^+$.

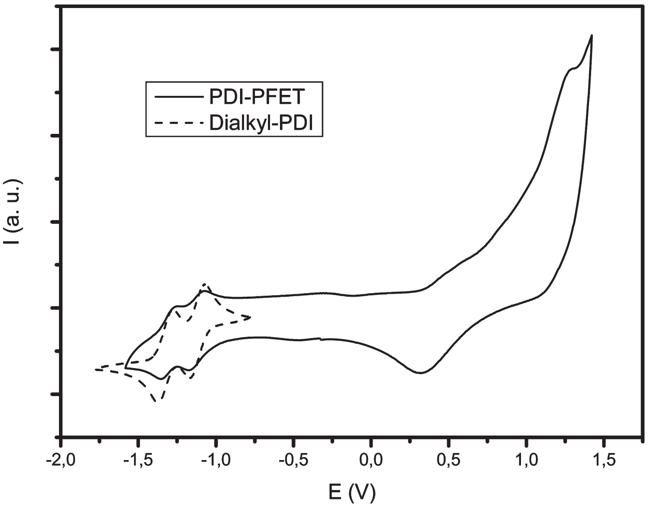

FIGURE 1. Cyclic voltammograms of the donor−acceptor polymer **PDI-PFET** along with reference **dialkyl-PDI** (in dichloromethane solutions, using platinum as working and counter electrode and tetrabutylammonium hexafluorophosphate (10^{-3} M) as supporting electrolyte; room temperature; scan rate: 200 mV/s. Values vs Fc/Fc$^+$).

Size exclusion chromatography (SEC, Table 1) in chloroform vs polystryrene standards revealed that the polymers have molecular weights (M_n) of 46 900 g/mol for **PDI-PFT** and 30 300 g/mol for **PDI-PFET**. Polydispersities of 4.6 and 5.2 were obtained, respectively, for the above-mentioned polymers. Differential scanning calorimetry (DSC) under nitrogen atmosphere at a heating rate of 10 deg/min showed a glass transition with an onset at 136 °C for **PDI-PFT** and 115 °C for **PDI-PFET**.

The alkyl side chains in the fluorene units and particularly those at the perylenediimide pendant moieties provide moderate solubility to these copolymers in common organic solvents, enabling their complete characterization by NMR, electrochemical, and optical techniques.

The structural similarity of functionalized copolymers **PDI-PFT** and **PDI-PFET**, i.e. they only differ in the spacer, is responsible for the many common features depicted on their NMR spectra. Thus, the ^{1}H NMR spectra of copolymers **PDI-PFT** and **PDI-PFET** show at low fields the expected signals of the pendant PDI units (~8.5 ppm) and around 5.2 ppm those corresponding to the protons directly linked to the imide nitrogen positions, similarly to monomer **10** (vide supra). Besides, the aromatic region also displays a series of relatively broadened signals arising from the fluorene, thiophene, and benzene fragments. The overlap of these signals prevents an unequivocal assignation. The spectra are completed with the signals, at high fields, arising from the alkyl chains of the structure. As would be expected, the ^{1}H NMR spectra of reference copolymers **PFT** and **PFET** only differ from those of their respective functionalized polymers in the absence of the signals of the pendant PDI moieties around 8.5 and 5.2 ppm and its alkyl chains. The ^{13}C NMR spectra of **PDI-PFT** and **PDI-PFET** show a good number of signals, some of them characteristic of the PDI moiety, for instance the imide carbonyl at around 164 ppm and the methylene directly linked to the imide nitrogen around 55 ppm. The signals corresponding to the carbon bridge on the fluorene moiety can also be seen at around 55 ppm, whereas the methylene groups directly linked to the carbon bridge are displayed at around 44 ppm. Additionally, the spectrum of the ethynylene-containing copolymer **PDI-PFET** displays weak signals around 83 ppm which can be assignad to the triple bond spacer, as is also the case for its reference copolymer **PFET**. The ^{13}C NMR spectra are finally completed with signals corresponding to the rest of the aromatic carbons and alkyl chains. The ^{13}C NMR spectra of reference copolymers **PFT** and **PFET** are very similar to that of the parent PDI-containing analogues, but obviously lacking the signals corresponding to the PDI rings. The FTIR spectra of copolymers **PDI-PFT** and **PDI-PFET** also evidence the presence in the structure of perylenediimide moieties, as the characteristic absorption pattern of the perylene skeleton with bands at 1580 and 1595 cm^{-1} and the absorption bands at 1658 and 1698 cm^{-1} indicating the presence of the imide group is clearly visible. On the other hand, the good accordance between the experimental and calculated elemental analysis ensures the good purity of our materials.

Electrochemistry. The electrochemical behavior of the donor−acceptor copolymers **PDI-PFT** and **PDI-PFET** and their respective reference copolymers **PFT** and **PFET** has been investigated by cyclic voltammetry in dichloromethane solutions and with platinum as the working and counter electrode, tetrabutylammonium perchlorate as supporting electrolyte, and a silver/silver chloride reference electrode. The measurements were carried out at room temperature and at a typical scan rate of 200 mV/s and the potentials were referenced versus the ferrocene/ferrocenium couple. The cyclic voltammograms of functionalized copolymers **PDI-PFT** and **PDI-PFET** (Figure 1) are not very well resolved, probably due to their moderate solubility, and show the amphoteric behavior of these materials. On the negative scan, the two one-electron reversible reduction waves characteristic of the perylenediimide moiety are clearly visible at around −1.12 and −1.30 V (Table 1). For comparison, the reference compound *N*,*N*′-(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide), **dialkyl-PDI**,[35] gives peaks at −1.11 and −1.31 V under the same conditions. Many perylenediimide derivatives substituted at the imide nitrogen have already been electrochemically investigated and it has been observed that the imide substituent has a negligible influence on the electronic properties of perylenediimides because of the presence of nodes of the HOMO and LUMO at the imide nitrogen.[36] Thus, perylenediimides can be regarded as closed chromophoric systems whose electronic properties remain

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(35) Demmig, S.; Langhals, H. *Chem. Ber.* **1988**, *121*, 225.
(36) Würthner, F. *Chem. Commun.* **2004**, 1564.

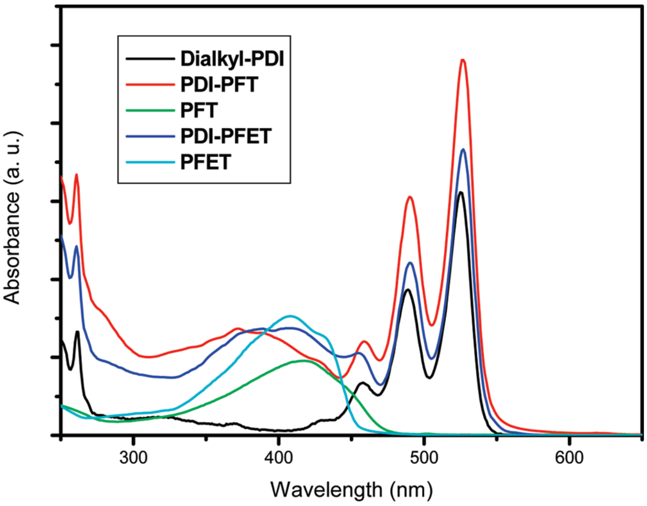

FIGURE 2. Absorption spectra of PDI-substituted polymers **PDI-PFT** and **PDI-PFET** along with references **PFT**, **PFET**, and **dialkyl-PDI** in dichloromethane solutions.

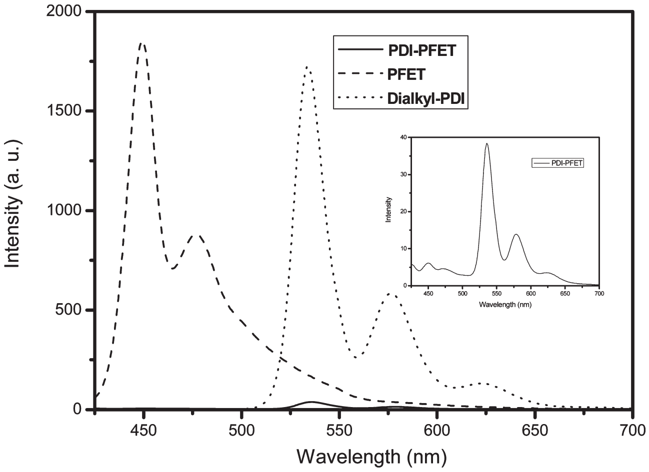

FIGURE 3. Fluorescence spectra of **PDI-PFET** along with references **PFET** and **dialkyl-PDI**, in dichloromethane. Inset: Magnified fluorescence spectrum of **PDI-PFET**.

unaltered by the imide substituent.[37] In this regard, in functionalized copolymers **PDI-PFT** and **PDI-PFET** no electronic influence of the perylenediimide moiety on the polymer main chain is expected as it is also observed in the UV−vis spectra (vide infra).

Toward positive values, the electrochemical response of functionalized polymers **PDI-PFET** and **PDI-PFT** is in general not well-resolved. However, a broad quasireversible oxidation wave can be identified in both cases, with an onset at around +0.33 V for **PDI-PFET** and +0.38 V for **PDI-PFT**. Reference copolymer **PFET** shows a broad and poorly resolved oxidation wave with onset at around +0.35 V.[38] A similar electrochemical behavior has been recorded for copolymer **PFT** (0.36 V).[39] For polymers **PDI-PFET** and **PFET**, an additional quasireversible oxidation wave around 1.29 V has been observed, probably arising from the ethynylene bonds.

The similar values observed for the oxidation and reduction processes of the two electroactive moieties in **PDI-PFET** and **PDI-PFT** compared to the reference materials suggest that there is no significant ground state interaction between the electron-donating polymer backbone and the electron-accepting PDI moieties.

Optical Properties. The UV−vis absorption spectra of the donor−acceptor copolymers **PDI-PFT** and **PDI-PFET** together with their respective references **PFT**, **PFET**, and **dialkyl-PDI** in diluted dichloromethane solutions are depicted in Figure 2. The absorption spectrum of the donor−acceptor polymers consists of the approximate superposition of the absorption features of its constitutive units (i.e., the conjugated backbone and the pendant perylenediimide units), confirming the minimal interaction between the chromophores in the ground state, in agreement with the electrochemical data. The spectra display absorption bands in the 350−450 nm region, arising from $\pi-\pi^*$ transitions in the conjugated polymeric backbone as it can be inferred by comparison to the reference polymers. Additionally, the absorption spectra of PDI-substituted polymers show the characteristic bands arising from the presence of the PDI side groups, with maxima at 526, 490, and 460 nm in dichloromethane.

Fluorescence emission spectra of PDI-functionalized polymers and their respective references were measured in diluted dichloromethane solutions at fixed optical density using the excitation wavelength corresponding to the absorption maxima of the conjugated backbone. The fluorescence properties of the polymer backbone in PDI-substituted copolymers **PDI-PFET** and **PDI-PFT** are greatly affected by the presence of the perylenediimide moiety. Thus, a strong quenching (>90%) of both the conjugated backbone fluorescent emission and the perylenediimide pendant groups was observed in these materials in comparison to the fluorescence spectrum of references **PFET** and **PFT** (Figure 3).

To explain this strong fluorescence quenching, two plausible explanations arise. On the one hand, one can expect a contribution of energy transfer from the π-conjugated backbone as it has a lower optical bandgap than the perylenediimide moiety, i.e., there is spectral overlap between the absorption spectrum of the p-conjugated backbone and the fluorescence spectrum of the PDI fragment. On the other hand, the electronic energy difference between the oxidation and reduction potential [$e(E_{\mathrm{ox}} - E_{\mathrm{red}})$] of the pendant donor−acceptor polymers is about 1.5−1.7 eV. Hence, photoinduced electron transfer from the conjugated backbone to the pendant electron accepting PDI moieties seems to be an energetically favorable relaxation process of the excited state for these polymers.

To find out if electron transfer is a likely process for **PDI-PFET** and **PDI-PFT** we can use the Weller eq 1.[40] We can use the oxidation potentials (+0.33 and +0.63 V vs Fc/Fc$^+$, respectively), the reduction potentials (−1.12 V vs Fc/Fc$^+$ in both cases), and the energy of the lowest excited singlet state, S_1, determined from the photoluminescence spectra of reference polymers (2.60 and 2.48 eV for **PDI-PFET** and **PDI-PFT**,

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[37] Langhals, H.; Demmig, S.; Huber, H. *Spectrochim. Acta* **1998**, *44A*, 1189.

[38] A value of +0.63 V vs Ag/Ag$^+$ has been reported for the oxidation onset of a similar PFET in film: Zhan, X.; Liu, Y.; Yu, G.; Wu, X.; Zhu, D.; Sun, R.; Wang, D.; Epstein, A. J. *J. Mater. Chem.* **2001**, *11*, 1606.

[39] A value of +0.97 V vs Ag/Ag$^+$ has been reported for the oxidation onset of PFT in film: Ranger, M.; Leclerc, M. *Can. J. Chem.* **1998**, *76*, 1571.

[40] Weller, A. Z. *Phys. Chem. Neue Folge* **1982**, *133*, 93.

respectively) to predict the Gibbs free energy for electron transfer from the conjugated backbone to the PDI moieties on the basis of the Weller equation:

$$\Delta G_{\mathrm{CS}} = -e[E_{\mathrm{ox}}(D) - E_{\mathrm{red}}(A)] + E(S_1) + \frac{e^2}{4\pi\varepsilon_0\varepsilon_{\mathrm{s}}R_{\mathrm{cc}}} + \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{r^+} + \frac{1}{r^-}\right)\left(\frac{1}{\varepsilon_{\mathrm{ref}}} - \frac{1}{\varepsilon_{\mathrm{s}}}\right) \qquad (1)$$

The radius of the PFET and PFT radical cations and the PDI radical anion are set to $r^+ = 5.0$ Å and $r^- = 4.7$ Å, respectively,[41,42] whereas the center-to-center chromophore distance (R_{cc}) was set at 10 Å, which is the maximum distance that can be reached.[43] The resulting values for ΔG_{CS} (-1.15 eV for **PDI-PFET** and -0.73 eV for **PDI-PFT**) predict that electron transfer from the conjugated polymer backbone to the accepting PDI units competes with energy transfer.

Conclusions

In this article we have presented a versatile route to the synthesis of polymers functionalized with electroactive perylenediimide units, which can be extended to other different moieties. Electrochemical investigations show that both electroactive units, the electron donor polymeric chain and the electron acceptor perylenediimide unit, preserve their nature in the ground state, which is confirmed by UV−vis spectroscopy. Fluorescence spectroscopy evidence a strong quenching of the intense fluorescence emission of the pendant perylenediimide, which is in accordance with the energy and/or electron transfer predicted by the Weller equation. Work is in progress to further investigate the photophysical processes taking place after the irradiation of these materials and their potential applications, as well as the introduction of other useful pendant structures.

Experimental Section

General. This section contains details for the synthesis of the reported novel compounds. General synthetic methods and the structural characterization of novel compounds described in this article are contained in the Supporting Information. 4′-Thien-3-ylbenzonitrile (**1**),[24] poly[2,7-(9,9-dioctylfluorene)-*alt*-2,5-thiophene] (**PFT**),[22] *N*-(9-octylnonyl)perylene-3,4:9,10-tetracarboxylic acid monoimide monoanhydride (**8**),[44] 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (**11**),[45] 2,7-diethynyl-9,9-dihexylfluorene (**13**),[46] and *N*,*N*′-(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**dialkyl-PDI**)[47] were prepared following previously reported synthetic procedures. All other chemicals were purchased from commercial sources and used as received without further purification unless otherwise specified. Solvents and reagents were dried by the usual methods prior to use and typically used under inert gas atmosphere.

2,5-Dibromo-3-(4′-cyanophenyl)thiophene (2). Under argon atmosphere, a solution of *N*-bromosuccinimide (2.48 g, 13.9 mmol) in 15 mL of anhydrous *N*,*N*-dimethylformamide is added dropwise to a solution of 4′-thien-3-ylbenzonitrile (**1**) (1.1 g, 5.9 mmol) in 25 mL of anhydrous *N*,*N*-dimethylformamide. The reaction crude is allowed to react at room temperature for 24 h and water is added slowly. The resulting mixture is stirred for 1 h and extracted with diethyl ether. The combined organic extracts are dried over anhydrous magnesium sulfate and vacuum evaporated. The remaining residue is purified by column chromatography (silica gel, hexane/dichloromethane 1/1) to give 2,5-dibromo-3-(4′-cyanophenyl)thiophene (**2**) as a white solid in 96% yield.

Mp 98 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.66 (AA′BB′ system, 2H, $J_1 = 8.57$ Hz, $J_2 = 1.94$ Hz), 7.55 (AA′BB′ system, 2H, $J_1 = 8.57$ Hz, $J_2 = 1.94$ Hz), 6.96 (s, 1H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 138.3, 132.2, 130.9, 129.1, 112.2; FTIR (KBr, cm^{-1}) ν 2926, 2855, 2227, 1661, 1499, 1020, 596; MS (EI, % I) 343 (M$^+$, 100), 183 (65). Anal. Calcd for $C_{11}H_5NSBr_2$: C, 38.51; H, 1.47; N, 4.08; S, 9.35. Found: C, 38.32; H, 1.36; N, 4.02; S, 9.18.

2,5-Dibromo-3-(4′-formylphenyl)thiophene (3). To a refluxing solution of 2,5-dibromo-3-(4′-cyanophenyl)thiophene (**2**) (1.96 g, 5.7 mmol) in 90 mL of dry dichloromethane is added a diisobutylaluminium hydride dichloromethane solution (1M, 6.0 mL, 6.0 mmol) dropwise over a period of 2 h under argon atmosphere. The solution is allowed to react at reflux temperature for 18 h and cooled to room temperature. Methanol is then carefully added until the reaction crude becomes a thick suspension. After careful addition of water, the reaction crude is treated with concentrated hydrochloric acid until complete solution and extracted with chloroform. The combined organic extracts are then washed with water and dried over anhydrous magnesium sulfate. After vacuum evaporation of the solvent, the remaining residue is purified by column chromatography (silica gel, hexanes/dichloromethane 1/1) to afford 2,5-dibromo-3-(4′-formylphenyl)thiophene (**3**) as a white solid in 93% yield.

Mp 76 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.99 (s, 1H), 7.88 (AA′BB′ system, 2H, $J_1 = 8.45$ Hz, $J_2 = 1.82$ Hz), 7.62 (AA′BB′ system, 2H, $J_1 = 8.45$ Hz, $J_2 = 1.82$ Hz), 6.99 (s, 1H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 191.5, 131.2, 129.8, 129.0; FTIR (KBr, cm^{-1}) ν 2923, 2834, 1682, 1604, 1423, 1214, 827, 811; MS (EI, % I) 346 (M$^+$,100), 238 (32), 158 (26), 113 (22). Anal. Calcd for $C_{11}H_6Br_2SO$: C, 38.18; H, 1.75; S, 9.26. Found: C, 38.36; H, 1.64; S, 9.32.

2,5-Dibromo-3-[4′-(hydroxymethyl)phenyl]thiophene (4). Sodium borohydride (92 mg, 2.43 mmol) is added portionwise to a solution of 2,5-dibromo-3-(4′-formylphenyl)thiophene (**3**) in 30 mL of anhydrous tetrahydrofuran under argon atmosphere. The reaction crude is stirred at room temperature for 24 h, and water is added. The mixture is extracted with diethyl ether and the combined organic extracts are dried over magnesium sulfate. After vacuum evaporation of the solvent, the residue is purified by a short column chromatography (silica gel, dichloromethane) to afford 2,5-dibromo-3-[4′-(hydroxymethyl)phenyl]thiophene (**4**) in 94% yield as a white solid.

Mp 134 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.49 (AA′BB′ system, 2H, $J_1 = 8.45$ Hz, $J_2 = 2.01$ Hz), 7.62 (AA′BB′ system, 2H, $J_1 = 8.45$ Hz, $J_2 = 2.01$ Hz), 7.00 (s, 1H), 4.74 (s, 1H), 4.71 (s, 1H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 140.5, 133.2, 131.4, 128.5, 126.8, 111.1, 107.6, 64.8; FTIR (KBr, cm^{-1}) ν 3384, 2922, 2853, 1635, 1506, 1423, 1409, 1043, 1017, 983, 811; MS (EI, % I):348 (M$^+$, 100), 238 (47), 160 (55). Anal. Calcd. for $C_{11}H_8Br_2SO$: C, 37.96; H, 2.32; S, 9.22. Found: C, 37.86; H, 2.27; S, 9.36.

2,5-Dibromo-3-[4′-(bromomethyl)phenyl]thiophene (5).[25] To a solution of 2,5-dibromo-3-[4′-(hydroxymethyl)phenyl]thiophene (**4**) (770 mg, 2.2 mmol) and triphenylphosphine (864 mg, 3.3 mmol)

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[41] It is difficult to estimate a radius for the PFET and PFT cations. We have used a radius of 5 Å, analogous to previous radii for conjugated systems of similar length, see ref 20a and: Peeters, E.; van Hal, P. A.; Knol, J.; Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C.; Janssen, R. A. J. *J. Phys. Chem. B* **2000**, *104*, 10174.

[42] The radius of the PDI anion was estimated from the density of *N*,*N*′-dimethylperylene-3,4:9,10-tetracarboxylic diimide determined from the X-ray crystallographic data: Hádicke, E.; Graser, F. *Acta Crystallogr. C* **1986**, *42*, 189.

[43] Estimated by semiempirical PM3 calculations, assuming a conformation with both electroactive units as separated as possible.

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[45] Dudek, S. P.; Pouderoijen, M.; Abbel, R.; Schenning, A. H. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2005**, *127*, 11763.

[46] Lee, S. H.; Nakamura, T.; Tsutsui, T. *Org. Lett.* **2001**, *13*, 2005.

[47] Demmig, S.; Langhals, H. *Chem. Ber.* **1988**, *121*, 225.

in 25 mL of anhydrous tetrahydrofuran, a solution of *N*-bromosuccinimide (587 mg, 3.3 mmol) in 10 mL of anhydrous tetrahydrofuran is slowly added over 20 min, under argon atmosphere and at room temperature. After 1 h, the reaction crude is filtered, the filtrate is evaporated under vacuum, and the residue is purified by column chromatography (silica gel, hexanes/dichloromethane 8/2) to afford 2,5-dibromo-3-[4′-(bromomethyl)-phenyl]thiophene (**5**) in 96% yield as a white solid.

Mp 65 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.65 (m, 4H), 7.15 (s, 1H), 4.53 (s, 2H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 141.3, 137.6, 134.2, 131.6, 129.2, 128.9, 111.5, 108.1, 33.0; FTIR (KBr, cm^{-1}) ν 2924, 2852, 1610, 1502, 1420, 1407, 1226, 1202, 1019, 806, 604; MS (EI, % I) 411 (M$^+$, 75), 330 (100), 250 (43), 171 (96), 127 (63). Anal. Calcd for $C_{11}H_7Br_3S$: C, 32.15; H, 1.72; S, 7.80. Found: C, 32.26; H, 1.95; S, 7.62.

2,5-Dibromo-3-(4′-hydroxyiminophenyl)thiophene (6). A solution of 2,5-dibromo-3-(4′-formylphenyl)thiophene (**3**) (1.0 g, 2.9 mmol), hydroxylamine hydrochloride (800 mg, 11 mmol), and pyridine (1 mL) in 35 mL of absolute methanol is heated at reflux temperature for 24 h under argon atmosphere. After vacuum evaporation of the solvent, the remaining residue is treated with water and chloroform. The organic phase is dried over anhydrous magnesium sulfate and evaporated under vacuum, to yield 2,5-dibromo-3-(4′-hydroxyiminophenyl)thiophene (**6**) in 98% yield as a white solid that can be used without additional purification.

Mp 176 °C; ^{1}H NMR (DMSO, 200 MHz) δ 11.33 (s, 1H), 8.12 (s, 1H), 7.62 (AA′BB′ system, 2H, J = 8.46 Hz), 7.53 (AA′BB′ system, 2H, J = 8.46 Hz), 7.36 (s, 1H); ^{13}C NMR (DMSO, 50 MHz) δ 147.7, 141.4, 134.0, 132.9, 132.3, 128.8, 126.6, 111.3, 107.7; FTIR (KBr, cm^{-1}) ν 3424, 3286, 2920, 2852, 1631, 1608, 1017, 976, 840, 812; MS (EI, % I) 361 (M$^+$, 100), 342 (25), 238 (26), 157 (20), 113 (16). Anal. Calcd for $C_{11}H_7Br_2SON$: C, 36.59; H, 1.95; N, 3.88; S, 8.88. Found: C, 36.36; H, 1.87, N, 3.66; S, 8.72.

2,5-Dibromo-3-[4′-(aminomethyl)phenyl]thiophene (7). Under argon atmosphere, lithium aluminum hydride (421 mg, 11 mmol) is added portionwise during 2 h to a refluxing solution of 2,5-dibromo-3-(4′-hydroxyiminophenyl)thiophene (**6**) (1.0 g, 2.8 mmol) in 45 mL of anhydrous toluene. The reaction crude is refluxed for 24 h, allowed to cool to room temperature, and first methanol, then water, and finally a 1 M hydrochloric acid aqueous solution are slowly added. The resulting mixture is then extracted with chloroform. The combined organic extracts are washed with water and dried over anhydrous magnesium sulfate. Vacuum evaporation of the solvent yields 2,5-dibromo-3-[4′-(aminomethyl)phenyl]thiophene (**7**) in 86% yield, which was used for the next step without further purification.

***N*-(9-Octylnonyl)perylene-3,4:9,10-tetracarboxylic Acid Bisimide (9).** Under argon atmosphere, a well-stirred suspension of *N*-(9-octylnonyl)perylene-3,4:9,10-tetracarboxylic acid monoimide monoanhydride (**8**) (315 mg, 0.5 mmol) and urea (4.5 g, 75 mmol) in 45 mL of anhydrous *N*,*N*-dimethylformamide is heated at reflux temperature for 24 h. After cooling to room temperature, water and an 1 M aqueous hydrochloric acid solution are added to the reaction crude. The resulting precipitate is filtered, and thoroughly washed with water and methanol. The collected solid is then dried under vacuum and purified by column chromatography (silica gel, dichloromethane/methanol 9.5/0.5) to afford *N*-(9-octylnonyl)perylene-3,4:9,10-tetracarboxylic acid bisimide (**9**) as a deep red solid in 64% yield.

Mp > 200 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.55 (br s, 8H), 5.11 (br m, 1H), 2.18 (br m, 2H), 1.81 (br m, 2H), 1.55 (s, 6H), 1.22−1.14 (m, 18H), 0.75 (t, 6H, J = 6.62 Hz); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 164.9 (w), 163.7 (w), 163.4, 135.7, 134.4, 132.2, 131.6, 131.1, 129.8, 127.2, 126.6, 124.6, 123.7, 123.3, 123.2, 55.3, 32.8, 32.2, 29.9, 29.9, 29.7, 27.4, 23.0, 14.5; FTIR (KBr, cm^{-1}) ν 2924, 2854, 1697, 1658, 1594, 1578, 1343, 1272, 853; MS (FAB) 628 (M$^+$). Anal. Calcd for $C_{41}H_{44}N_2O_4$: C, 78.31; H, 7.05; N, 4.45. Found: C, 78.35; H, 7.00; N, 4.56.

2,5-Dibromothiophene Monomer 10. By Direct Imidation. A mixture of *N*-(9-octylnonyl)perylene-3,4:9,10-tetracarboxylic acid bisimide (**8**) (210 mg, 0.33 mmol), 2,5-dibromo-3-[4′-(aminomethyl)phenyl]thiophene (**7**) (476 mg, 1.32 mmol), Zn(OAc)$_2$ (48 mg, 0.26 mmol), and 2 g of imidazol is heated at 180 °C during 2 h under argon atmosphere. After cooling to room temperature, the mixture is treated with 100 mL of an aqueous 10% hydrochloric acid solution. The solid is collected by filtration, washed with another portion of acid solution, then thoroughly washed with water and finally with methanol. The remaining solid is dried under vacuum and further purified by flash chromatography (silica gel, dichloromethane) to yield **10** as a deep red solid in 84% yield.

By N-Alkylation. Under argon atmosphere, a mixture of *N*-(9-octylnonyl)perylene-3,4:9,10-tetracarboxylic acid bisimide (**9**) (150 mg, 0.23 mmol), 2,5-dibromo-3-[4′-(bromomethyl)phenyl]thiophene (**5**) (294 mg, 0.71 mmol), potassium carbonate (317 mg, 2.3 mmol), and a catalytic amount of sodium iodide in 30 mL of anhydrous *N*,*N*-dimethylformamide are heated at 130 °C for 12 h The reaction crude is allowed to cool to room temperature and then water and a 1 M aqueous hydrochloric acid solution are added. The resulting precipitate is filtered and thoroughly washed with water and methanol. The collected solid is dried under vacuum and purified by column chromatography (silica gel, dichloromethane) to afford 2,5-dibromothiophene monomer **10** as a deep red solid in 86% yield.

Mp > 200 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.66−8.58 (m, 8H), 7.63−7.33 (m, 11H), 5.43 (s, 2H), 5.21 (s, 1H), 2.27 (br s, 4H), 1.90 (br s, 8H), 1.77−1.69 (br m, 8H), 1.36−1.04 (m, 36H), 0.85 (t, 12H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 164.9 (w), 163.7, 142.0, 137.3, 135.2, 134.5, 133.8, 132.00, 131.9, 131.4, 129.8, 129.7, 129.0, 126.7, 126.6, 124.5, 123.5, 123.3, 111.6, 108.1, 55.3, 43.8, 32.8, 32.2, 30.00, 29.9, 29.7, 27.4, 23.0, 14.5; FTIR (KBr, cm^{-1}) ν 2924, 2854, 1698, 1658, 1595, 1580, 1337, 851; MS (FAB): 958 (M$^+$), 721. Anal. Calcd for $C_{52}H_{50}Br_2N_2O_4S$: C, 65.14; H, 5.25; N, 2.92; S, 3.34. Found: C, 64.86; H, 5.61; N, 2.48; S, 3.07.

Polymer PDI-PFT. A mixture of 2,5-dibromothiophene monomer **10** (95 mg, 0.1 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**11**) (63 mg, 0.1 mmol), and tetrakis(triphenylphosphine)palladium (0) (2 mg, 2×10^{-3} mmol) in a deareated mixture of 22 mL of tetrahydrofuran and 18 mL of a 2 M potassium carbonate aqueous solution was heated at reflux temperature under argon atmosphere for 72 h. The thick reaction mixture was allowed to cool to room temperature and methanol was added to give an abundant precipitate. The solid was collected, dissolved in chloroform, and precipitated out of methanol again. The polymer was further purified by washing with acetone in a Soxhlet apparatus for 24 h to remove small molecules, oligomers, and catalyst residues. The final product was dried under vacuum to afford polymer **PDI-PFT** as a deep red solid in 82% yield.

^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.68−8.46 (br m, 8H), 7.68−7.50 (AA′BB′ system, 2H, J = 8.19 Hz), 7.39 (AA′BB′ system, 2H, J = 8.19 Hz), 6.88 (m, 1H), 5.33 (s, 2H), 5.12 (br m, 1H), 2.17 (b, 8H), 1.82 (s, 12H), 1.13−0.96 (m, 36H), 0.75 (br s, 12H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 163.8, 142.4, 136.3, 135.7, 135.7, 135.2, 134.6, 132.0, 131.5, 131.5, 130.1, 129.9, 129.6, 129.5, 127.0, 126.7, 126.6, 123.6, 123.3, 120.7, 110.6, 55.5, 55.2, 53.8, 43.9, 40.7, 32.8, 32.2, 32.2, 30.4, 30.1, 30.0, 29.9, 29.6, 27.4, 24.1, 23.0, 22.9, 14.5; FTIR (KBr, cm^{-1}) ν 2924, 2852, 1697, 1658, 1594, 1333, 811. Anal. Calcd for $C_{81}H_{90}N_2O_4S$: C, 81.92; H, 7.64; N, 2.36; S, 2.70. Found: C, 82.03; H, 7.42; N, 2.64; S, 2.56. SEC (vs PS) M_n = 46 900 g/mol; M_w = 10 200 g/mol; pd = 4.6.

Polymer PDI-PFET. A mixture of 2,5-dibromothiophene monomer **10** (96 mg, 0.1 mmol), 2,7-diethynyl-9,9-dioctylfluorene (**12**) (44 mg, 0.1 mmol), bis(triphenylphosphine)palladium(II) dichloride (5 mg, 4.4×10^{-3} mmol), copper iodide (6 mg, 0.03 mmol), triphenylphosphine (30 mg, 0.11 mmol), and diisopropylamine (2.0 mL) in 35 mL of deareated anhydrous toluene was heated at reflux temperature for 72 h under argon atmosphere. The reaction mixture was allowed to cool to room temperature and slowly added into methanol to give a precipitate. The solid was collected, dissolved in chloroform, and precipitated out of methanol again. The polymer was further purified by washing with acetone in a Soxhlet apparatus for 24 h to remove small molecules, oligomers, and catalyst residues. The final product was dried under vacuum to afford polymer **PDI-PFET** as a deep red solid in 80% yield.

^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.70−8.63 (br m, 8H), 7.88−7.47 (br m, 11H), 5.50 (br s, 2H), 5.12 (br s, 1H), 2.26 (br m, 2H), 1.97 (br m, 4H), 1.58 (s, 6H), 1.13−0.98 (m, 24H), 0.74 (s, 12H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 163.8, 151.7, 142.4, 141.0, 137.7, 135.4, 134.7, 134.6, 132.1, 132.1, 131.1, 131.0, 129.8, 128.5, 127.4, 126.9, 126.3, 126.0, 124.5, 123.9, 123.6, 123.4, 120.5, 82.1, 55.7, 55.2, 43.9, 40.6, 32.8, 32.2, 32.2, 30.4, 29.9, 29.6, 27.4, 24.1, 23.0, 14.5; FTIR (KBr, cm^{-1}) ν 2926, 2855, 1699, 1661, 1596, 1466, 1439, 1406, 1337, 853. Anal. Calcd for $C_{85}H_{90}N_2O_4S$: C, 82.62; H, 7.34; N, 2.27; S, 2.59. Found: C, 82.36; H, 7.55; N, 2.07; S, 2.23. SEC (vs PS) M_n = 30 300 g/mol; M_w = 5 800 g/mol; pd = 5.2.

Polymer PFET. A mixture of 2,5-dibromothiophene (48 mg, 0.2 mmol), 2,7-diethynyl-9,9-dioctylfluorene (**12**) (88 mg, 0.2 mmol), bis(triphenylphosphine)palladium(II) dichloride (8 mg, 6.5×10^{-3} mmol), copper iodide (9 mg, 0.03 mmol), triphenylphosphine (60 mg, 0.2 mmol), and diisopropylamine (2.0 mL) in 35 mL of deareated anhydrous toluene was heated at reflux temperature for 72 h under argon atmosphere. The reaction mixture was allowed to cool to room temperature and slowly added into methanol to give a precipitate. The solid was collected, dissolved in chloroform, and precipitated out of methanol again. The polymer was further purified by washing with acetone in a Soxhlet apparatus for 24 h to remove small molecules, oligomers, and catalyst residues. The final product was dried under vacuum to afford polymer **PFET** as a yellow solid in 94% yield.

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.71 (s, 2H), 7.50 (br s, 4H), 7.29 (s, 2H), 2.01 (s, 1H, 4H), 1.67 (s, 4H), 1.24 (s, 12H), 0.85 (s, 8H), 0.64 (s, 6H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 151.6, 141.9, 141.4, 141.2, 132.5, 132.3, 132.1, 131.1, 130.6, 127.7, 127.6, 127.4, 126.2, 125.6, 125.2, 121.8, 121.7, 121.0, 120.7, 120.5, 113.5, 95.6, 95.5, 83.4, 83.2, 55.7, 40.7, 32.2, 30.4, 29.6, 24.1, 23.0, 14.5; FTIR (KBr, cm^{-1}) ν 2925, 2852, 1636, 1462, 1417, 820, 799. Anal. Calcd for $C_{52}H_{50}Br_2N_2O_4S$: C, 97.36; H, 1.08; S, 0.82. Found: C, 97.66; H, 0.96; S, 1.02. SEC (vs PS) M_n = 75 900 g/mol; M_w = 26 200 g/mol; pd = 2.9.

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Supporting Information Available: General experimental procedures and compound characterization for all new compounds along with copies of key spectra. This material is available free of charge via the Internet at http://pubs.acs.org.