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PAPER

Synthesis and properties of small band gap thienoisoindigo based conjugated polymers

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Using Stille and Suzuki polymerization reactions we incorporate thienoisoindigo (TII) as an acceptor co-monomer into a series of alternating π -conjugated copolymers with combinations of benzene, thiophene and carbazole as donor co-monomers. By changing the nature and length of the donor segments, the optical band gap of these soluble TII copolymers can be varied over a large range from 1.52 eV down to 0.87 eV. The semiconducting properties of the TII copolymers were established in bottom-gate bottom-contact field-effect transistors that provide hole mobilities for these materials in the range of 10^{-3} to 10^{-2} cm² V⁻¹ s⁻¹.

Introduction

Semiconducting polymers form the active functional material in organic field-effect transistors (FETs) and organic photovoltaic (OPV) cells. For designing new conjugated polymers for these applications, several parameters must be considered. The most relevant electronic parameters are the optical band gap, redox levels and charge carrier mobility, but material properties such as solubility, molecular weight and tendency to form ordered aggregates or semi-crystalline domains are likewise important. The leading design motif for controlling the optical band gap and energy levels of conjugated semiconducting polymers is the alternation of electron rich and electron deficient units along the chain as pioneered by Havinga^{1,2} and Tanaka.³ For the electron rich unit conjugated oligomers are often used. These commonly include benzene, thiophene, pyrrole and furan or combinations thereof as building blocks, sometimes in fused ring configurations. For the electron deficient unit, aromatic heterocycles such as quinoxaline, benzothiadiazole and thienopyrazine that contain electron withdrawing nitrogen atoms have been effective.4-6

In recent years, the incorporation of cyclic amides or diimides has been established as a very effective way to combine strong electron accepting properties with a tendency to provide close intermolecular packing. This favours small optical band gaps and high charge carrier mobilities and has resulted in exceptionally good performance in FETs and OPV cells.^{7,8} Examples of these new acceptor units are diketopyrrolopyrrole,^{9–11} benzodipyrrolidiones,¹² thienopyrroledione,^{13–15} and isoindigo^{16–19} as shown in Fig. 1.

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Fig. 1 Structures of pyrrolo[3,4-*c*]pyrrole-1,4-dione (or diketopyrrolopyrrole, DPP), benzo[1,2-*b*:4,5-*b*']dipyrrole-2,6(1*H*,5*H*)-dione (BDPD), thieno[3,4-*c*]pyrrole-4,6-dione (TPD), isoindigo (II) and thienoisoindigo (TII).

Isoindigo based small molecules^{16,20} and polymers^{17,21-27} show great potential for OPV, as do isoindigo derived materials for FETs²⁸ and organic memory devices.²⁹ Replacing the benzene ring of isoindigo with a thiophene to give a thienoisoindigo (TII) might further enhance planarity along the backbone resulting in better packing and higher mobilities for both holes and electrons. The potential for such materials was recently shown for a TIIbenzothiadiazole copolymer.³⁰

Here we present the synthesis of five new TII-copolymers in which TII alternates with benzene, thiophene, carbazole or combinations thereof and we explore this new class of TII-based materials for their semiconducting properties. The TII copolymers show band gaps in the range of 0.87-1.52 eV and mobilities in the range of 10^{-3} to 10^{-2} cm² V⁻¹ s⁻¹ in bottom-gate bottom-contact FETs.

Results and discussion

Synthesis

The synthesis of the TII monomer starts with an Ullmann coupling of 3-bromothiophene (1) with 2-hexyldecan-1-amine to give **2** (Scheme 1),^{30,31} followed by a Friedel–Crafts reaction with oxalyl chloride to give the thiophene derivative of isatin (3). The



Scheme 1 (i) CuI, DMAE, 90 °C; (ii) Et_3N , DCM, 0 °C; (iii) Lawesson's reagent, toluene, 65 °C; (iv) NBS, DCM 0 °C; (v) Pd_2dba_3 , PPh_3 , K_3PO_4 , Aliquat 336, toluene–H₂O, 115 °C; (v) NBS, DCM, 0 °C.

isatin derivative was dimerised with Lawesson's reagent to give 4, following a procedure previously used for various pyrrole-2,3diones.³² This procedure is known to give exclusively the *E* isomer, which is confirmed for 4 by six sp² carbon signals in the ¹³C NMR spectrum indicating a single isomer and a single IR band at 1667 cm⁻¹ of the C=O stretch vibration. For the *Z* isomer symmetrical and anti-symmetrical vibrations would be expected. Bromination of the coupled product 4 with NBS provided the TII-monomer 5 as a dark purple solid. Using 5 an extended TII-derivative was made by coupling 3-dodecylth-iophene *via* a Suzuki reaction and bromination of the product 6 with NBS to give the dark blue TII-monomer 7.

Based on monomers 5 and 7 a series of new TII-based polymers was synthesized *via* Stille and Suzuki couplings using different co-monomers (Scheme 2). PTIIT and PTII3T were synthesized by Stille coupling with 2,5-bis(trimethylstannyl)thiophene because polymerization reactions with thiophene tend to give higher molecular weights with Stille reactions compared to Suzuki polymerizations.³³ For the co-polymerisations aimed at incorporating benzene (PTIIP and PTIITPT) or carbazole (PTIICb) the Suzuki coupling generally gives higher molecular weights. All polymerization reactions used end-capping with mono-functionalized thiophene stannanes and bromides or phenyl boronic acid pinacol esters and bromobenzenes depending on the type of polymerization to remove reactive end groups.³⁴

In many optoelectronic applications of conjugated copolymers the molecular weight is a critical factor because it controls the morphology and interchain ordering in the material. For PTIITPT, PTIICb and PTII3T the molecular weight was determined with GPC to be respectively $M_n = 32400 \text{ g mol}^{-1}$, 33 100 g mol⁻¹ and 13 400 g mol⁻¹ versus polystyrene standards with PDIs of 2.5, 2.5 and 4.0 as summarized in Table 1. For PTIIT and PTIIP, GPC measurements of the molecular weight gave inconclusive results because these polymers showed a strong interaction with the column material. The three copolymers,



PTIITPT, PTIICb and PTII3T, that do not suffer from this problem have extra side chains attached to the donor units probably inhibiting the interaction with the column.

Optical and electrochemical properties

Fig. 2 shows the UV-vis-near IR absorption spectra of the TIIbased copolymers in solution and as thin films on glass. The absence of a bathochromic shift in these polymers between the solution and thin film samples shows that they have a strong tendency to aggregate in solution. The optical band gaps for these materials, measured as the onset of absorption, range from 0.87 eV for the PTIIT polymer to 1.52 eV for the PTIICb polymer (Table 1). Relevant optical data for thienoisoindigo (PTIIX) polymers from this work and isoindigo (PIIX) polymers available from the literature are collected in Table 1 and reveal that the optical band gaps of PTIIX derivatives are smaller than that of PIIX. The difference is very pronounced for PTIIT ($E_g =$ 0.87 eV) and PIIT ($E_g =$ 1.65 eV (ref. 21)). For none of these polymers significant fluorescence could be observed.

Cyclic voltammetry (CV) was used to determine the onsets of oxidation and reduction potentials *versus* the Fc/Fc^+ redox couple of the co-polymers in solution (Fig. 3). Using the redox potentials the HOMO and LUMO levels were estimated using

 Table 1
 Molecular weight, optical and electrochemical data of the TII-based and II-based copolymers

Polymer	$M_{\rm n}/{ m g~mol}^{-1}$	PDI	$\lambda_{\rm max}^{\rm sol}/{\rm nm}$	$E_{\rm g}^{\rm sol}/{\rm eV}$	$E_{\rm g}^{\rm film}/{\rm eV}$	$E_{\rm ox}{}^a/{\rm V}$	$E_{\rm red}^{a}/V$	$E_{\rm g}^{{ m cv}b}/{ m eV}$	E _{HOMO} ^c /eV	$E_{\rm LUMO}^{c}/{\rm eV}$	Ref.
Thienoisoindigo pol	vmers (PTII-X)									
PTIIT	n/a	n/a	1006	0.92	0.87	-0.41	-1.45	1.04	-4.82	-3.78	
PTIIP	n/a	n/a	872	1.21	1.18	-0.24	-1.60	1.36	-4.99	-3.63	
PTIICb	33 100	2.5	746	1.57	1.52	0.01	-1.49	1.50	-5.24	-3.74	
PTII3T	13 400	4.0	768	1.36	1.29	-0.20	-1.51	1.31	-5.03	-3.72	
PTIITPT	32 400	2.5	742	1.53	1.45	-0.20	-1.48	1.28	-5.03	-3.75	
Isoindigo polymers	$(PII-X)^d$										
PIIT (PT-ID1) ^e	17 200	2.1	684	1.68	1.65	0.69			-5.92		21
PIICb (PCzID) ^e	8956	1.5	576	1.80	1.75	0.43	-1.20	1.63	-5.66	-4.03	23
PII3T (P3TI) ^e	73 000	2.9	645	1.63	1.50	0.48	-1.18	1.66	-5.71	-4.05	19

^{*a*} Onsets, potentials *vs.* Fc/Fc^+ . ^{*b*} $E_g^{\text{cv}} = e(E_{\text{ox}} - E_{\text{red}})$. ^{*c*} $E = -5.23 - eE_{\text{redox}}$. ^{*d*} Values may differ slightly from those stated in the cited papers due to small corrections (*e.g.* for reference potentials) made to allow direct comparison. ^{*e*} The acronyms used in the cited references are included between parentheses. Values for the isoindigo polymers were measured for thin films in ref. 19, 21 and 23.



Fig. 2 Normalized absorption spectra of TII-based polymers in chloroform solution (a) and as thin films on glass (b).

 $E = -5.23 - eE_{\rm redox}$ ³⁵ The results are summarized in Table 1. The high HOMO levels for PTIIT (-4.82 eV) and to a lesser extend for PTIIP (-4.99 eV), PTII3T (-5.03 eV) and PTIITPT (-5.03 eV) make these polymers strong electron donors that can easily be oxidized. PTIICb is the only polymer that has a somewhat deeper HOMO (-5.24 eV). Compared to the corresponding isoindigo (II) analogues PIIT (PT-ID1,²¹ -5.92 eV), PIICb (PCzID,²³ -5.66 eV) and PII3T (P3TI,¹⁹ -5.71 eV), which were measured as thin films, a large difference of up to 1.1 eV for the HOMO level is observed.

The differences between optical and electrochemical properties of the thienoisoindigo and isoindigo polymers are induced by the stronger electron donating properties of the thiophene ring compared to the benzene ring. In addition, co-planarity with the neighbouring aromatic units is easier whilst steric hindrance is reduced, especially when a phenyl or carbazole is used as an aromatic unit adjacent to isoindigo.



Fig. 3 Cyclic voltammetry of TII-based polymers recorded in ODCB with $NBu_4^+PF_6^-$ as a supporting electrolyte.

Electrical characterization

We investigated the electrical transport of conjugated polymers discussed above in field-effect transistors. In the transfer curves of the polymers PTIIT, PTIIP, PTIITPT, PTII3T and PTIICb measured immediately after spin-coating, *i.e.* prior to thermal annealing, a large hysteresis was observed and the threshold voltage was not at zero gate bias. After annealing the transistors at 180 °C overnight, the performance improved for all polymers except PTIIT. We note that for small band gap polymers often ambipolar transport is observed and has been reported for a related TII based conjugated polymer.³⁰ In the FETs of PTII-X we observed hole transport but no electron transport. Fig. 4 shows the typical transfer characteristics of a ring transistor for the four other polymers measured at room temperature after annealing. The curves for PTIIP, PTIITPT, PTII3T and PTIICb show almost no hysteresis and have threshold voltages at zero voltage as well as high on-off ratios with a current modulation of almost five to six decades for all these four copolymers.



Fig. 4 Linear ($V_D = -2$ V) and saturated ($V_D = -20$ V) transfer characteristics of a spin-coated field-effect transistor. The channel length is 40 µm and channel width is 1000 µm. To prevent parasitic leakage currents, ring geometry was used in all cases. (a) PTIIP, (b) PTIITPT, (c) PTII3T and (d) PTIICb.

The linear and saturated mobilities are quite similar and are about 5×10^{-3} cm² V⁻¹ s⁻¹ for PTIIP, 8×10^{-3} cm² V⁻¹ s⁻¹ for PTIITPT, 2×10^{-3} cm² V⁻¹ s⁻¹ for PTII3T and 5×10^{-3} cm² V⁻¹ s⁻¹ for PTIICb.

Conclusion

A first series of TII based π -conjugated polymers has been synthesized, extending the class of polymers incorporating an amide functionality as an acceptor in their backbone. The TII unit influences the energy levels significantly when compared to isoindigo polymers by raising the HOMO levels and therewith lowering the optical band gap to as low as 0.87 eV. The FET mobilities are in line with other well performing polymers showing that these amide derived materials can be valuable in many organic electronic devices.

Experimental section

General procedures

All starting materials and reagents were purchased from commercial suppliers unless stated otherwise. All ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Varian Mercury Spectrometer using CDCl₃ as solvent with tetramethylsilane (TMS) as an internal standard. The given values are in ppm relative to TMS (0 ppm). UV-vis-near IR optical absorption spectra were recorded on a Perkin-Elmer Lambda 900

spectrometer in a chloroform solution in a quartz cell or as a thin film spin coated on a glass substrate. Cyclic voltammetry (CV) was conducted under an inert atmosphere using an Autolab PGSTAT30 with a three electrode setup equipped with a platinum disc working electrode, a silver counter electrode and a silver electrode coated with silver chloride (Ag/AgCl) as a quasi reference electrode in combination with ferrocene/ferrocenium (Fc/Fc^{+}) as an internal standard. A 1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in ortho-dichlorobenzene (ODCB) was used as the electrolyte. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) was measured on a PerSeptive Biosystems Voyager - DE PRO spectrometer using either a-cyano-4-hydroxycinnamic acid (CHCA) and/or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrices. Molecular weights of the polymers were determined with two high temperature GPC setups, a Shimadzu LC-20AD Prominence Liquid Chromatograph equipped with a SPD-20A UV-Vis detector and a RID-10A refractive index detector and a Mixed-D (200-400 000 Da versus polystyrene standards) column running on chloroform at 110 °C and a PL-GPC 120 High temperature Chromatograph with a Mixed-C (200-2 000 000 Da versus polystyrene standards) column using ODCB at 80 °C as eluent. FETs were fabricated on a heavily doped silicon wafer as a common gate electrode, covered by 200 nm thermally grown silicon dioxide passivated with HMDS as a gate dielectric and gold source and drain electrodes were defined using conventional photolithography and a 10 nm Ti adhesion layer. The polymers were applied via spin coating at 1000 rpm for 30 s with an acceleration of 100 rpm per s in chloroform solution and thermally annealed for 24 h at 180 °C in vacuum before measuring. The electrical transport was measured using a HP 4155C semiconductor parameter analyzer in vacuum of 10^{-6} mbar. To compare the current all measurements were done on a 40 µm channel length and a channel width of 1000 µm.

2-Hexyldecan-1-amine

Triphenylphosphine (36.5 g, 139 mmol) and phthalimide (20.5 g, 139 mmol) were suspended in DCM and cooled to 0 °C. Then 2hexyl-1-decanol (30.6 g, 126.4 mmol) was added and stirred for 30 min before the dropwise addition of diisopropyl azodicarboxylate (28.1 g, 139 mmol) while maintaining the temperature under 10 °C. Upon the complete addition the mixture was stirred for another one hour at room temperature before it was concentrated in vacuo. After redissolving in hexanes and filtration the resulting oil was subjected to a short silica column and concentrated. Then hydrazine and THF were added and the mixture was refluxed overnight. After cooling 2 M KOH was added and the product was extracted with ethyl acetate, washed with brine and dried over MgSO₄ before the crude oil was subjected to distillation. The product was distilled at 180 $^{\circ}$ C and 2 \times 10^{-1} mbar to give 17.3 g (57%) 2-hexyldecan-1-amine as a colourless oil. ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.60 (d, J = 4.7Hz, 2H), 1.36–1.18 (m, 25H), 1.08 (s, 2H), 0.88 (t, J = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 45.25, 40.93, 31.88, 31.54, 30.09, 29.76, 29.61, 29.32, 26.78, 26.75, 22.66, 14.08.

N-(2-hexyldecyl)thiophen-3-amine (2)

A mixture of 3-bromothiophene (1) (11.023 g, 67.6 mmol), 2hexyldecan-1-amine (16.3 g, 67.6 mmol), copper(I) iodide (1.3 g, 6.8 mmol) and grinded potassium phosphate tribasic (43.0 g, 200 mmol) in dimethylaminoethanol (30 ml) was heated to 90 °C for 2 days under an argon atmosphere. The reaction was cooled to room temperature and filtered. The residue was washed with ethyl acetate and the filtrate was concentrated and subjected to silica column chromatography (gradient heptanes-dichloromethane 0-100%) to give 7.7 g (35.5%) of the desired air sensitive compound. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.13 (dd, J =5.1, 2.9 Hz, 1H), 6.61 (dd, J = 5.1, 1.5 Hz, 1H), 5.91 (dd, J = 3.0, 1.5 Hz, 2H), 3.56 (s, 1H), 2.97 (d, J = 6.0 Hz, 2H), 1.70–1.52 (m, 1H), 1.45–1.12 (m, 24H), 0.88 (t, J = 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 149.10, 124.94, 119.90, 94.76, 49.87, 37.82, 32.22, 32.21, 31.90, 31.88, 30.07, 29.74, 29.60, 29.33, 26.79, 26.76, 22.69, 22.68, 14.10.

4-(2-Hexyldecyl)-4H-thieno[3,2-b]pyrrole-5,6-dione (3)

To a solution of 20 ml dichloromethane and oxalyl chloride (2.6 ml, 30 mmol) was added dropwise a solution of N-(2-hexyldecyl) thiophen-3-amine (2) (7.7 g, 24 mmol) in dichloromethane (40 ml) while cooling the reaction at 0 °C. After 30 min a solution of triethylamine (6 ml) in dichloromethane (40 ml) was added dropwise after which the reaction was warmed to room temperature and stirred overnight. The mixture was concentrated and purified by silica column chromatography using a heptanes-dichloromethane 70: 30 mixture as eluent to give 5.9 g of 4-(2-hexyldecyl)-4H-thieno[3,2-b]pyrrole-5,6-dione as an orange oil in 70% yield. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.00 (d, J = 5.0 Hz, 1H), 6.76 (d, J = 4.7 Hz, 1H), 3.53 (d, J = 7.4Hz, 2H), 1.81–1.74 (m, 1H), 1.36–1.18 (m, 24H), 0.87 (td, J = 6.8, 2.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 172.96, 165.50, 161.72, 143.77, 113.11, 111.01, 46.44, 36.96, 31.83, 31.73, 31.38, 29.88, 29.55, 29.47, 29.24, 26.34, 26.31, 22.63, 22.59, 14.08, 14.04.

(*E*)-4,4'-bis(2-hexyldecyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (4)

Lawesson's reagent (1.9 g, 4.72 mmol) was put under argon and a solution of 4-(2-hexyldecyl)-4H-thieno[3,2-b]pyrrole-5,6-dione (3) (3.342 g, 9.44 mmol) in dry toluene (20 ml) was added. The reaction was heated to 65 °C and stirred until complete conversion was seen on TLC. After cooling, water was added and the product was extracted with chloroform, washed with brine and dried over MgSO₄. After removal of the solvent the crude product was subjected to silica column chromatography with hexanes-dichloromethane as eluent to give 1.238 g of the title compound in 36.3% yield. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.52 (d, J = 5.1 Hz, 2H), 6.78 (d, J = 5.1 Hz, 2H), 3.69 (d, J = 7.4Hz, 4H), 1.93-1.85 (m, 2H), 1.35-1.21 (m, 48H), 0.92-0.81 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 171.28, 151.51, 134.19, 121.04, 114.20, 111.32, 46.12, 37.13, 31.87, 31.85, 31.76, 31.46, 29.93, 29.60, 29.49, 29.25, 26.40, 26.37, 22.68, 22.64, 22.61, 14.09, 14.05. MALDI-TOF m/z: 722.43 (M⁺, 100%). FT-IR: 1667 cm^{-1} (C=O).

(*E*)-2,2'-dibromo-4,4'-bis(2-hexyldecyl)-[6,6'-bithieno[3,2-*b*] pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (5)

To a solution of (*E*)-4,4'-bis(2-hexyldecyl)-[6,6'-bithieno[3,2-*b*] pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (**4**) (280 mg, 0.53 mmol) in dichloromethane was added *N*-bromosuccimide (189 mg, 1.06 mmol) at 0 °C. Upon completion the reaction mixture was washed with water and brine and dried over MgSO₄ before it was purified over a silica column with a heptanes–chloroform mixture to give 366 mg of the desired monomer (79% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 6.81 (s, 2H), 3.62 (d, *J* = 7.4 Hz, 4H), 1.87–1.78 (m, 2H), 1.38–1.19 (m, 48H), 0.91–0.82 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 170.20, 150.07, 122.97, 119.50, 114.88, 114.62, 46.13, 37.19, 31.86, 31.77, 31.41, 31.38, 29.93, 29.62, 29.50, 29.28, 26.34, 22.66, 22.63, 14.10, 14.07. MALDI-TOF *m*/*z*: 880.26 (M⁺, 100%).

(*E*)-2,2'-bis(4-dodecylthiophen-2-yl)-4,4'-bis(2-hexyldecyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (6)

Under an argon atmosphere toluene (3 ml), water (0.3 ml) and one drop of Aliquat 336 were added to (E)-2,2'-dibromo-4,4'-bis(2hexyldecyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'(4H,4'H)-dione (5) (100 mg, 114 µmol), 2-(4-dodecylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (171.7 mg, 454 µmol) and potassium phosphate tribasic (106 mg, 500 µmol). Then argon was bubbled through for 30 min before adding tris(dibenzylideneacetone)dipalladium(0) (4.6 mg, 5 µmol) and triphenylphosphine (3.3 mg, 12.5 µmol). The reaction mixture was heated to 115 °C and stirred overnight. After extraction with chloroform and water the organic fraction was washed with brine and dried over MgSO₄ before it was subjected to column chromatography using a heptanes-chloroform gradient. Product containing fractions were combined to give 123 mg of the title compound (88% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.25 (s, 2H), 6.93 (s, 2H), 6.80 (s, 2H), 3.63 (d, J = 7.4 Hz, 4H), 2.61 (t, J = 7.8 Hz, 4H), 1.87 (s, 2H), 1.64 (q, J = 7.2 Hz, 4H), 1.47–1.05 (m, 84H), 0.99– 0.67 (m, 18H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 170.59, 151.36, 145.04, 144.72, 137.40, 125.61, 120.36, 118.81, 113.27, 107.03, 45.77, 37.15, 31.95, 31.91, 31.84, 31.40, 30.46, 30.44, 30.00, 29.72, 29.68, 29.57, 29.52, 29.40, 29.38, 29.36, 26.34, 26.32, 22.70, 22.69, 13.88. MALDI-TOF m/z: 1222.86 (M⁺, 100%).

(*E*)-2,2'-bis(5-bromo-4-dodecylthiophen-2-yl)-4,4'-bis(2-hexyldecyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (7)

A solution of (*E*)-2,2'-bis(4-dodecylthiophen-2-yl)-4,4'-bis(2-hexyldecyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)dione (6) (123 mg, 100.7 µmol) in dichloromethane (4 ml) was cooled to 0 °C and wrapped in aluminium foil. Then *N*-bromosuccimide (36.23 mg, 201.3 µmol) was added. When complete conversion was observed by TLC the solvent was removed *in vacuo* and the crude product was subjected to silica column chromatography with heptanes–dichloromethane 75/25 to give 107 mg of the extended monomer (76.8% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.03 (s, 2H), 6.62 (s, 2H), 3.61 (dt, *J* = 7.4, 3.9 Hz, 4H), 2.53 (t, *J* = 7.6 Hz, 4H), 1.80 (p, *J* = 6.5 Hz, 2H), 1.60 (p, *J* = 7.2 Hz, 4H), 1.45–1.23 (m, 42H), 0.95–0.80 (m, 18H). MALDI-TOF *m*/*z*: 1378.66 (M⁺, 100%).

PTIIT

To a mixture of monomer 5 (99 mg, 112.7 umol) and 2.5-bis-(trimethylstannyl)thiophene (46.2 mg, 112.7 µmol) under an argon atmosphere were added dry toluene (2 ml) and dry dimethylformamide (0.2 ml). Argon was bubbled through for 30 min before addition of tris(dibenzylideneacetone)dipalladium(0) (4.1 mg, 4.5 µmol) and triphenylphosphine (2.4 mg, 9 µmol) and heating the reaction mixture to 110 °C. After 2 h subsequently tributyl(thiophen-2-yl)stannane (42 mg, 112.7 µmol) and 2-bromothiophene (37 mg, 225.2 µmol) were added with 30 min interval to end cap the polymer. After another 30 min the reaction mixture was cooled, precipitated in acetone and filtered through a Soxhlet thimble. The polymer was extracted with acetone, hexanes, dichloromethane and chloroform. The dichloromethane fraction was concentrated to a minimal amount, precipitated in methanol, filtered over a PTFE filter and dried in a vacuum oven at 40 °C to give 85 mg of the title polymer. GPC (both in chloroform at 110 °C and in ODCB at 80 °C) was inconclusive as the polymer had interaction with the column. λ_{max} (CHCl₃) = 1006 nm.

Synthesis of PTIIP

To a mixture of 5 (49.5 mg, 56.4 µmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (18.6 mg, 56.4 µmol) and potassium phosphate tribasic (48 mg, 225.6 µmol) under an argon atmosphere were added toluene (0.8 ml), 0.1 ml demi water (0.1 ml) and a 50:50 mixture of toluene and Aliquat 336 (0.1 ml). Argon was bubbled through this solution for 30 minutes before addition of tris(dibenzylideneacetone)dipalladium(0) (2.75 mg, 3 µmol) and triphenylphosphine (2 mg, 8 µmol). The reaction was started in a preheated oil bath at 115 °C and stirred at that temperature for 3 h. Then subsequently 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (46 mg, 225.6 µmol) and bromobenzene (48 µL, 451.2 µmol) were added with 30 min intervals to end cap the polymer. After another 30 min the reaction was cooled and quenched by precipitation in methanol (100 ml). The polymer was redissolved in chloroform and stirred overnight with diethylthiocarbamate solution (4 g 1^{-1} , 50 ml). After extraction the organics were washed with water, concentrated to a minimal amount and precipitated in methanol. The precipitates were filtered through a Soxhlet thimble and extracted under argon with methanol, heptanes, dichloromethane and chloroform. The dichloromethane fraction contained most of the polymer and was precipitated in methanol after which the precipitates were filtered over a PTFE filter and dried in a vacuum oven at 40 °C to give 36 mg of the dark polymer. GPC (both in chloroform at 110 °C and in ODCB at 80 °C) was inconclusive as the polymer had interaction with the column. λ_{max} (CHCl₃) = 872 nm.

PTIICb

To a mixture of monomer **5** (72 mg, 82.0 μ mol), 9-(heptadecan-9yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (53.9 mg, 82.0 μ mol) and potassium phosphate tribasic (87 mg, 410 μ mol) were added, under an argon atmosphere, toluene (3 ml) and water (0.3 ml) together with one drop of Aliquat 336. Argon was bubbled through for 30 minutes before addition of tris(dibenzylideneacetone)dipalladium(0) (3.0 mg, 3.3 µmol) and triphenylphosphine (1.7 mg, 6.6 µmol) after which the reaction was heated to 115 °C for 3 h. Then subsequently 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (16.7 mg, 82.0 µmol) and bromobenzene (17.3 µl, 164 µmol) are added with 30 min interval to end cap the polymer. After another 30 minutes the reaction was cooled and quenched by precipitation in acetone. Filtration through a Soxhlet thimble and subsequent extraction with acetone, hexanes and chloroform gave most of the polymer in the chloroform fraction. Reducing the volume and precipitation in methanol followed by filtration over a PTFE filter and drying the polymer. GPC (CHCl₃, 110 °C): $M_n = 33\ 100\ g mol^{-1}$ and PDI = 2.3. λ_{max} (CHCl₃) = 746 nm.

PTII3T

To monomer 7 (52 mg, 39.2 µmol) and 2,5-bis(trimethyl-stannyl) thiophene (16.06 mg, 39.2 µmol), under an argon atmosphere, were added dry toluene (3 ml) and dry dimethylformamide (0.6 ml). Argon was bubbled through for 30 minutes before tris(dibenzylideneacetone)dipalladium(0) (1.44 mg, 1.57 µmol) and triphenylphosphine (1.03 mg, 3.9 µmol) were added. The reaction was heated to 110 °C and stirred overnight. Then the polymer was end capped subsequently with tributyl(thiophen-2yl)stannane (14.9 mg, 40 µmol) and 2-bromothiophene (13 mg, 80 µmol) in 30 min interval. After another one hour the reaction was cooled, precipitated in methanol and filtered through a Soxhlet thimble and washed with acetone. The polymer was subjected to Soxhlet extraction under an argon atmosphere with acetone, hexanes and chloroform to give 33 mg of the desired polymer. GPC (CHCl₃, 110 °C): $M_n = 13400 \text{ g mol}^{-1}$ and PDI = 4.0. GPC (ODCB, 80 °C): $M_n = 14\ 300\ \text{g mol}^{-1}$ and PDI = 2.1. λ_{max} (CHCl₃) = 768 nm.

PTIITPT

To monomer 7 (45.2 mg, 32.7 µmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (10.8 mg, 32.7 µmol) and K_3PO_4 (27.8 mg, 130.8 µmol) under an argon atmosphere was added THF : H₂O 5 : 1 (3.6 ml). Argon was bubbled through this solution for 15 minutes after which Pd₂dba₃ (1.2 mg, 1.3 µmol) and ${}^{t}Bu_{3}PHBF_{4}$ (0.8 mg, 2.6 µmol) were added. The mixture was then heated to 80 °C and stirred overnight at this temperature. Then bromobenzene (27.5 µl, 261.6 µmol) was added 1 h after the addition of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (26.7 mg, 130.8 µmol) to terminate all reactive end groups. After 1 h the reaction was quenched by precipitating the polymer in methanol including the solids that had already formed in the reaction mixture. After filtration the residue was subjected to Soxhlet extraction with acetone, heptanes, dichloromethane, chloroform, chlorobenzene and ortho-dichlorobenze. Approximately 20 mg of the polymer remained as solids in the Soxhlet timble. The chloroform fraction was concentrated to give 2 mg of the desired polymer. (CHCl₃, 110 °C): $M_n = 29500 \text{ g mol}^{-1}$ and PDI = 2.5. GPC (ODCB, 80 °C): $M_n = 32400 \text{ g mol}^{-1}$ and PDI = 2.5. λ_{max} (CHCl₃) = 737 nm.

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