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Complete List of Authors:	DELBOSC, Nicolas; CEA, INAC Yahya, Wan Zaireen Nisa; CEA, INAC LEMAITRE, Noëlla; CEA, LITEN-INES Berson, Solenn; CEA, LITEN-INES FUCHS, Franz; CEA, INAC GREVIN, Benjamin; CNRS, UMR5819 SPrAM FAURE-VINCENT, Jérôme; CEA, INAC TRAVERS, Jean-Pierre; CEA, INAC/SPrAM DEMADRILLE, Renaud; CEA, INAC

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PAPER

Synthesis, optoelectronic and photovoltaic properties of conjugated alternating copolymers incorporating 2,1,3-benzothiadiazole or fluorenone units: a comparative study

Nicolas Delbosc,[a] Wan Zaireen Nisa Yahya,[a] Noella Lemaitre[b], Solenn Berson,[b] Franz Fuchs[a], Benjamin Grévin,[a] Jérome Faure-Vincent[a], Jean-Pierre Travers[a] and Renaud Demadrille*[a]

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A series of p-type alternating copolymers based on oligothiophene and fluorene electron-donating units, and fluorenone or benzothiadiazole electron-withdrawing units was synthesised via Suzuki coupling reaction. Their optical, electrochemical and photovoltaic properties were investigated in details allowing to draw the rational rules of the structure-properties relationships. We highlight in this work the crucial role of the side solubilizing groups attached to the polymer backbones that have a significant impact on the morphology of the blends and the solar cells power conversion efficiency. Devices with an active area of 0.28 cm², based on fluorenone-copolymers and [70]PCBM blends showed Voc up to 0.95V and Power Conversion Efficiencies (PCE) up to 1.82% under AM1.5 simulated sunlight (100 mW.cm^{-2}) conditions. These values are improved compared to the ones reported to date with this class of materials.

Introduction

Polymers solar cells (PSCs) have received during the last ten years tremendous attention because they offer numerous advantages such as low cost, light weight, flexibility, short energy payback time, and solution processability[1-4]. Among multiple examples of π-conjugated polymers[5-6], polythiophenes are one of the most promising materials for organic bulk-heterojunction (BHJ) solar cells due to their good thermal and chemical stability, as well as for their unique electronic and optical properties.[7-9] The most widely known example of thiophene-based polymers in the photovoltaic field is poly(3-hexylthiophene) P3HT, which in combination with fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester ([60]PCBM) in photovoltaic devices, has achieved a power conversion efficiency up to 4-5% after extensive optimisation.[10] However P3HT, with a band gap of 1.9-2.0 eV, can absorb a limited range of wavelengths up to 650 nm, which represents only 22.4% of influx photons of the solar spectrum.[11] To improve the photovoltaic performances of PSCs one widely used approach consists in decreasing the band gap of conjugated polymers in order to increase the total amount of photons that they can harvest from the sun. A powerful strategy to broader the absorption spectra of conjugated polymers consists in the combination of alternating electron donating groups and electron withdrawing groups (D-A) in the polymer backbone.[12] In addition the use of appropriate building blocks for the polymer design could lead to a low-lying highest occupied molecular orbital (HOMO) energy level of the macromolecules that gives rise to a high open circuit voltage (V_{OC}) of BHJ solar cells.[13] One of the most popular electron-withdrawing building blocks to prepare D-A copolymers is the 2,1,3-benzothiadiazole unit. It exists several hundreds of papers reporting the use of benzothiadiazole-based copolymers in PSCs. This unit can be combined to various electron donating segments to achieve medium band gap[14] or small band gap copolymers[15] revealing high power conversion efficiencies up to 6%.[2]

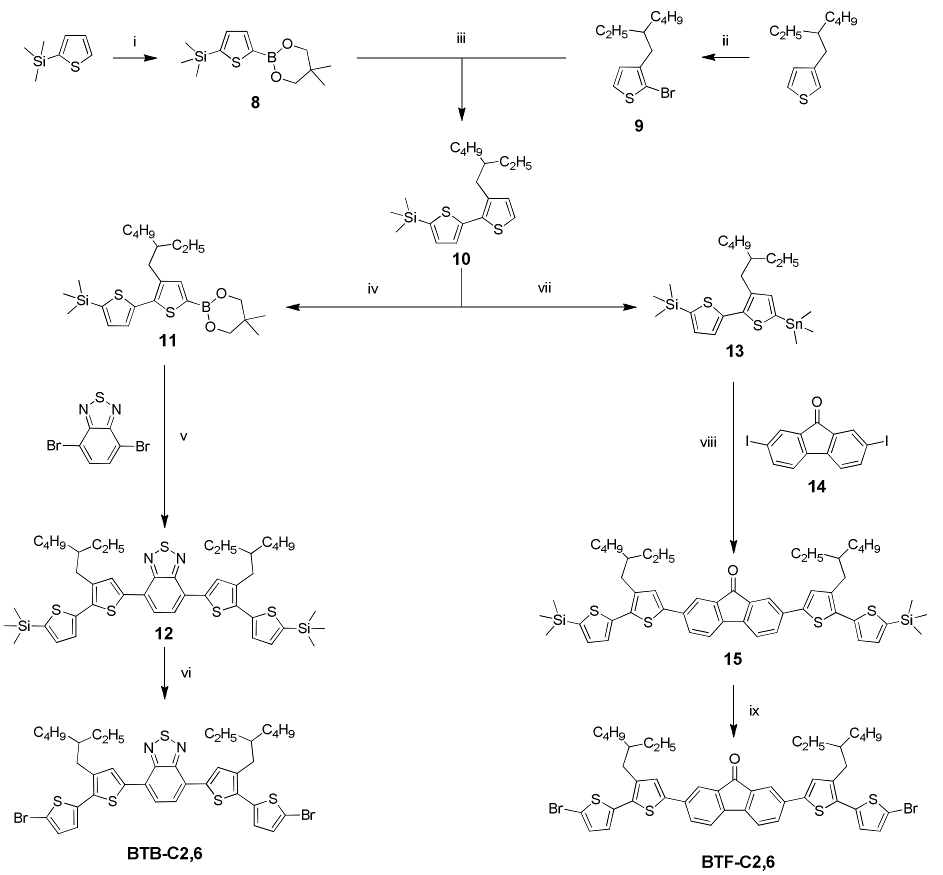
In contrast the literature concerning the use of fluorenone unit for the preparation of polymers suitable for applications in BHJ solar cells is really scarce[16] and up to now their maximum power conversion efficiencies are limited to 1.5%.[17]

In this work we compare rationally the potential of these two electron withdrawing building blocks, i.e 2,1,3-benzothiadiazole and fluoren-9-one, when they are incorporated in polymer backbones for an application in solar cells. We have investigated a class of regioregular alternating copolymers combining bithiophene and fluorene units as donating segments and 2,1,3-benzothiadiazole or fluorenone as electron-withdrawing units named respectively **PBTFB** and **PBTFF**. The combination of fluorene to bithiophene is expected to lead to macromolecules showing low-lying HOMO energy levels.[18] Previous works have thoroughly described the key role of the solubilizing alkyl chains attached to the polymer backbone on the macromolecular properties and the device performances.[18b,c] Therefore to complete our investigations we have synthesized two types of polymers, bearing either linear alkyl chains or branched alkyl chains. We present the synthesis of these copolymers and their optoelectronic features. We report also our preliminary investigations on the photovoltaic properties of these copolymers in typical BHJ devices with [70]PCBM.

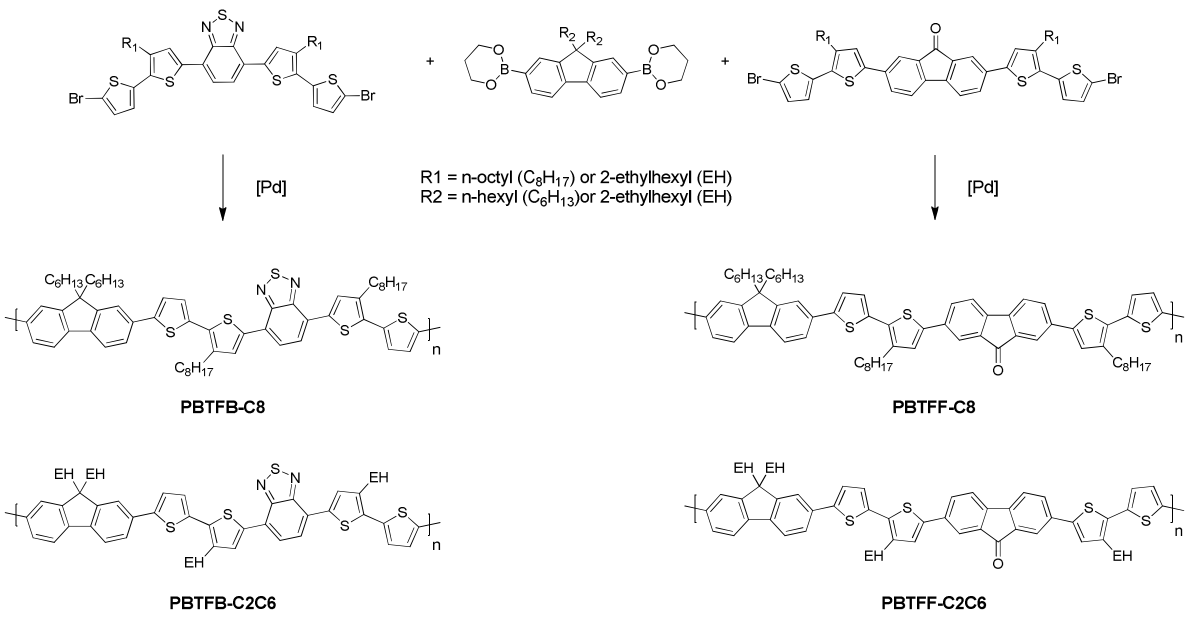
Results and discussion

Synthesis and characterization of the polymers

For the preparation of the copolymers, the key intermediates are symmetric precursors based on the central electron-withdrawing units and two bithiophene segments. The macromonomers 2,7-bis(5'-bromo-4-octyl-5,2'-bithien-2-yl)-fluorenone[19] abbreviated as **BTF-C8** and 4,7-bis(5'-bromo-3-octyl-2,2'-bithiophen-5-yl) benzo[c][1,2,5]thiadiazole, abbreviated as **BTB-C8** were prepared using a linear synthetic strategy[18b,19] starting from commercially available products: 2,7-dibromo-fluoren-9-one and 2,5-dibromo-2,1,3-benzothiadiazole. The synthetic route towards these macromonomers involves iterative Suzuki coupling reactions and halogenation reactions using either N-iodosuccinimide or N-bromosuccinimide. The preparation of these intermediates can be found in ESI file. For the preparation of 2,7-bis(5'-bromo-4-(2-ethylhexyl)-5,2'-bithien-2-yl)-fluorenone abbreviated as **BTF-C2,6** and its benzothiadiazole-containing analogue, namely 4,7-bis(5'-bromo-3-2-ethylhexyl-2,2'-bithiophen-5-yl)-benzo[c][1,2,5]thiadiazole abbreviated as **BTB-C2,6**, we have developed a convergent synthesis which is described in Scheme 1. This new, efficient and versatile synthetic route is based on the preparation of a bithiophene intermediate. This key intermediate can be boronated or stannylated and then coupled using palladium cross-coupling reactions respectively according to Suzuki or Stille conditions to 2,7-diiodo-fluoren-9-one (synthesized in the laboratory) and 2,5-dibromo-2,1,3-benzothiadiazole (commercially available). One advantage of using this synthetic scheme relies on the use of a similar precursor for the preparation of **BTF-C2,6** and **BTB-C2,6.** Besides, the purification of the silylated compounds (**12** and **15**) is facilitated. We found that Suzuki conditions allow us to obtain **12** but after work-up and purification by chromatography on silica gel, 30 % of the protected bithiophene was recovered. A deboronation reaction presumably occurs because of the electron donating character of alkylated bithiophene. For this reason, alternatively for the preparation of **BTF-C2,6**, Stille conditions were used affording the expected compound in higher yields.



Scheme 1: Convergent synthesis of fluorenone (**BTF-C2,6**) and benzothiadiazole (**BTB-C2,6**) based monomers with ramified alkyl chains.
i. 1) ^{t}BuLi, -78°C, THF, 2) $B(OMe)_3$, -50°C to rt, 3) HCl 0,1M, 4) Neopentylglycol, $MgSO_4$, Et_2O, 63%; ii. NBS, $CHCl_3$, rt, 88%; iii. $Pd_2(dba)_3$, tBu_3P, K_2CO_3 1M, THF, 70°C, 88%; iv. 1) ^{t}BuLi, -78°C, THF, 2) $B(OMe)_3$, -50°C to rt, 3) HCl 0,1M, 4) Neopentylglycol, $MgSO_4$, Et_2O, 51%; v. $Pd(PPh_3)_4$, K_2CO_3 1M, Toluene/THF (1/1 vol.), 85°C, 32%; vi. NBS, $CHCl_3$, 0°C to rt, 45%; vii. 1) ^{t}BuLi, -78°C, THF, 2) $ClSnMe_3$, 85%; viii. Pd(PPh3)4, Toluene/DMF (1:1 vol.), 63%; ix. NBS, $CHCl_3$, 0°C to rt, 94%.



Scheme 2: Synthetic routes toward the copolymers. Conditions of polymerization are for polymers containing linear alkyl chain, $Pd_2(dba)_3$, (o-tolyl)phosphine, Toluene, Na_2CO_3 (2M), reflux 72h; and for polymers with ramified alkyl chain, $Pd(PPh_3)_4$, Toluene, K_2CO_3 1M, 100°C, 36h.

With the different precursors, the alternating pi-conjugated copolymers comprising either 2,1,3-benzothiadiazole or fluorenone units in their backbone and differing by their solubilising groups were prepared by polycondensation reaction of the synthesized precursors and 2,2'-(9,9-dialkyl-9*H*-fluorene-2,7-diyl)-bis(1,3,2-dioxaborinane) according to Suzuki coupling conditions (Scheme 1). After their synthesis, the polymers were precipitated in methanol and the unreacted monomers, and small oligomers are removed by Sohxlet extraction using acetone. To characterize the synthesized polymers we analyzed their macromolecular parameters by Size Exclusion Chromatography (SEC) (Table 1) in THF at 40°C.

Polymers	Mn ($kg.mol^{-1}$)	Mw ($kg.mol^{-1}$)	PDI Mw/Mn
PBTFB-C8 (a)	5.6	8.6	1.54
PBTFB-C2C6 (a)	8.7	15.1	1.74
PBTFF-C8 (a)	3.2	5.0	1.56
PBTFF-C2C6 (a)	4.8	7.4	1.52
PBTFF-C2C6 (b)	8.0	14.4	1.81
PBTFF-C2C6 (c)	29.3	72.3	2.47

Table 1. Macromolecular parameters of the copolymers measured against polystyrene standards after soxhlet fractionation and extraction with chloroform, polymerization in toluene (a), in DMF-Toluene 20-80 in volume (b) and in DMF-Toluene 50-50 in volume (c).

The rather low molecular weights of **PBTFB-C8** and **PBTFF-C8** can be explained by the linear nature of the solubilizing groups which limits the solubility, additionally we found that the **PBTFF** copolymers show lower solubility in the reaction mixture leading to shorter polymer chains. This can be related to the presence of the fluorenone which rigidifies the polymer backbone[19b] and promotes aggregation of polymer chains.

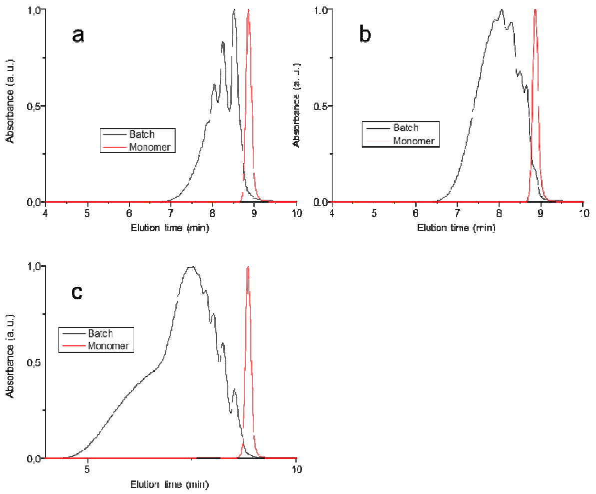


Figure 1: Elugram of monomer (red lines) and batches of **PBTFF-C2C6** (black lines**).** Polymerization reaction under different solvent conditions: toluene only (a), toluene and DMF 80/20 in volume (b), toluene and DMF 50/50 in volume (c).

In order to investigate more into details the influence of the solvent of reaction on the macromolecular parameters and to achieve higher molecular weights for the fluorenone-based copolymers, we have carried out the polymerization reaction of the **BTF-C2,6** monomer with the bis-boronic fluorene derivative under various conditions. The Suzuki reaction was carried out in toluene or in a more polar mixture of toluene and DMF (80/20 or 50/50 in volume). Indeed, Suzuki-Myaura coupling reactions are known to perform well if weak bases such as K_2CO_3 are associated to DMF[20].

It's important to note that the purity of the monomers, their concentration and the catalyst are exactly the same in these three experiments. The corresponding SEC elugrams are reported in Figure 1.
The SEC traces clearly demonstrate that increasing the polarity of the solvent has a strong effect on the polymerization reaction and the macromolecular parameters of the copolymers. It appears that the batches of polymers are in fact composed of short oligomers and high molecular weight fractions. In the first elugram (a), several peaks at high retention times are predominant. These peaks correspond to short oligomers and the amount of high molecular weight polymer chains remains low. When the polarity of the solvent is increased by adding 20% of DMF in volume, the quantity of low molecular weight oligomers decreases and the number of higher molecular weight chains largely increases (b). When 50% of DMF in volume is added, a bimodal distribution appears corresponding to the formation of high molecular weight polymer chains (c). After soxhlet extraction of the remaining oligomers using acetone, hexane and dichloromethane, high molecular weight fractions of the polymers can be extracted using chloroform. By modifying the polarity employing a mixture of solvent for the polymerization reaction, we demonstrate that the Mn values of the chloroform fractions of the polymers can be significantly increased from 5 kDa to almost 30 kDa.

Optical and electrochemical properties.

The UV-Vis absorption spectra of **PBTFB** and **PBTFF** in dilute choloroform solutions and their neat films are illustrated in Figure 3. UV-Vis absorption data are summarized in Table 2. **PBTFF** absorbs broadly in the 350-600 nm region, with a strong absorption band and a shoulder whereas **PBTFB** shows two distinct absorption bands. A similar absorption band is found for the four polymers in the 400-420 nm region corresponding to π-π* transitions of aromatic rings of the donating units. The additional absorption features in the visible range originate from an intramolecular charge transfer (ICT) transition. This ICT band is located in the 500-700 nm range for benzothiadiazole-containing copolymers and it appears as a shoulder in the 500-650 nm region for the fluorenone based copolymers. The enhanced absorption intensity in the visible region and the red-shifted absorption spectra that are displayed for **PBTFB** compared to **PBTFF** may be related to the quinoidal nature of the benzothiadiazole (BTD) unit inducing a better delocalization of the electrons.
The absorption spectra for both **PBTFB** and **PBTFF** in solid films were red shifted as compared with their solution spectra (Fig. 2). A greater red shift of the absorption spectra was observed for polymers bearing linear alkyl chains in solid state as compared with their solution. This behaviour is related to a smaller distance between the chains resulting in better π-π stacking interactions.[18c] The larger spectral shifts (approximately 40 nm at the longer wavelength) were observed in the case of **PBTFF** and this behaviour may be attributed to the more planar nature of the fluorenone unit that probably facilitates the packing of the conjugated backbone through a better chain planarization[19b].

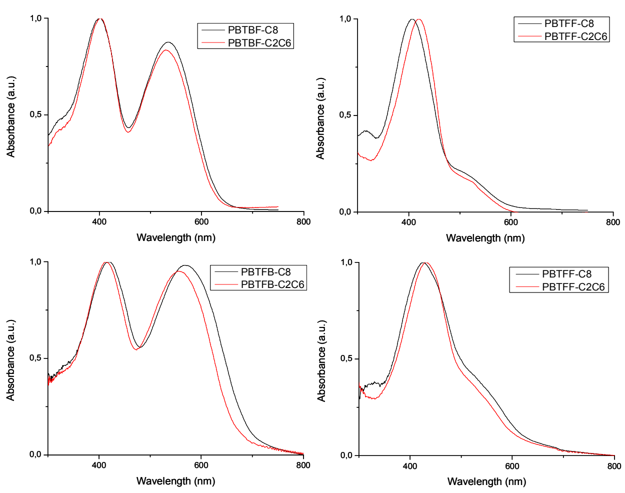


Figure 2: UV-Vis spectra of polymers containing benzothiadiazole (left) or fluorenone (right) in solution in $CHCl_3$ (top) and at the solid state, spin-coated from chlorobenzene solution on glass substrates (bottom).

Cyclic voltammetry analysis (CV) of polymers in thin films were performed to estimate their electronic energy levels positions. Polymer films were drop-casted on a platinum working electrode from chlorobenzene solutions and the experiments were carried out in acetonitrile containing 0.1 M n-Bu_4NPF_6 as the supporting electrolyte. A platinum wire was utilized as the counter electrode and all potentials were recorded versus Ag/AgCl calibrated using a ferrocene/ferrocenium (Fc/Fc^+) redox couple. HOMO and LUMO energy levels of the polymers were estimated from the onset of oxidative and reductive peak.
All the polymers show deep HOMO energy levels ranging from -5.31 to -5.67eV. The introduction of the dialkyl-fluorene unit between the bithiophene units, diminishes the electron delocalization over the donating segments and is clearly responsible for the lowering of the HOMO energy levels compared to quaterthiophene-benzothiadiazole[21] (E_{HOMO} = -5.2 eV) or quaterthiophene-fluorenone[17] (E_{HOMO} = -5.0 eV) alternating copolymers. The LUMO energy levels of our polymers are lying between -3.20 and -3.37 eV giving a ΔE of 0.4-0.7 eV with the LUMO level of the fullerenes. Indeed, the LUMO energy levels of [60]PCBM and [70]PCBM were measured under the same experimental conditions by CV and they were estimated lying at -3.90 eV and -3.80 eV respectively. This energetical difference is sufficiently large to generate a driving force that guarantees electron transfer in a blend of these polymers with PCBM. Interestingly, we observed lower HOMO energy levels by *circa* 0.12-0.15eV for polymers bearing branched alkyl chains (**PBTFB-C2C6** and **PBTFF-C2C6)** relative to their corresponding analogs bearing linear chains. This observation can be considered as another clear manifestation of a better packing of the backbone in the solid state for the polymers bearing linear solubilizing groups.[18c] A better packing induces better π-stacking interactions and decreases the oxydation potential of the polymers in the solid state. Therefore smaller electrochemical

Polymers	λ_{max} [(a)] solution (nm)	λ_{max} [(b)] film (nm)	$E_g^{opt\,(c)}$ (eV)	$E_{ox\ onset}$ (V)	$E_{red\ onset}$ (V)	E_{HOMO} [(d)] (eV)	E_{LUMO} [(d)] (eV)	E_g^{elect} (eV)
PBTFB-C8	403, 535	418, 568	1.75	0.51	-1.62	-5.31	-3.19	2.12
PBTFB-C2C6	402, 530	418, 555	1.82	0.73	-1.52	-5.53	-3.28	2.25
PBTFF-C8	408, 509	426, 550	1.91	0.62	-1.52	-5.42	-3.28	2.14
PBTFF-C2C6	419, 505	430, 555	2.00	0.87	-1.43	-5.67	-3.37	2.30

Table 2. Optical and electrochemical data of polymers. Electrochemical data are obtained in polymer films obtained by dropcasting from chlorobenzene solution on Pt electrode. (a) Measured in chloroform solution. (b) Film spin-coated from chlorobenzene solution. (c) Optical band gap, $Eg_{opt} = 1240/(\lambda_{onset})$ film. (d) Potentials determined by cyclic voltammetry in 0.10 M Bu_4NPF_6/CH_3CN. Orbital energy level are estimated by comparison with ferrocene oxidation measured at 0.28 V.

bandgaps (2.12-2.14eV) are found for **PBTFB-C8** and **PBTFF-C8** compared to **PBTFB-C2C6** and **PBTFF-C2C6** (2.25-2.30eV). Taking into account the deep HOMO energy levels of our polymers and the LUMO energy level of the fullerenes, high V_{OC} values are expected for the devices using these polymers in combination with fullerenes. The higest V_{OC} values should be obtained for the devices based on **PBTFB-C2C6** and **PBTFF-C2C6**.

Solar cell applications.

To investigate the potential use of the copolymers in photovoltaic applications, bulk-heterojunction solar cells were fabricated by spin-coating the **PBTFB** or **PBTFF**/[70]PCBM chlorobenzene solutions onto the PEDOT:PSS spin coated ITO glass, followed by deposition of Ca/Al or TiO_2/Al as the cathode. Current density-voltage (*J-V*) curves of the devices were measured under simulated AM1.5G illumination (1000W.m^{-2}) and the photovoltaic parameters of the devices, *i.e.* short circuit current (*J*sc), open circuit voltage (*V*oc), fill factor (FF), and PCE are summarized in Table 3. In order to report power conversion efficiencies for solar cells with a high accuracy and a good reproducibility, it is crucial to avoid solar cells with small active areas (typically below 0.2 cm^2). For this reason, in this study the effective device area was 0.28 cm^2 (+/-0.02 cm^2). Indeed it is known that efficiencies obtained on smaller areas are size dependent and can be strongly overestimated[22] due to fringing electrical effects that are responsible for the collection of current outside the perimeter of the electrode[22c] or due to the size-dependent variation of the series resistance of the ITO layer[22d].

In order to carry out a rational comparison of the photovoltaic performances of the polymers and to draw reliable conclusions, fractions of polymers of comparable Mn (between 3 and 8 KDa) were used for the fabrication of the blends with fullerenes. Indeed it is now well-known that macromolecular parameters have a strong effect on the performances of the devices. High molecular weight fractions allow the formation of stacked aggregates and produce better interconnections within the bicontinuous network resulting in the enhancement of the charge transport and higher PCE.[23]

Preliminary investigations (See ESI) were carried out using [60]PCBM as electron acceptor compound. However maximum PCE of 1.16% and 0.80% with current densities below 5mA.cm-² were obtained for blends based on **PBTFB** and **PBTFF** polymers respectively. [60]PCBM was then replaced by [70]PCBM, since it exhibits a better absorption in the visible part of the spectrum that might contribute to the generation of charges. This would help to increase the current densities delivered by the solar cells. Different blend ratios of polymers and [70]PCBM were screened to optimize the device performances (Table 3).

Active layer With [70]PCBM	Ratio D:A	Voc/ (V)	J_{sc} (mA.cm^{-2})	FF	PCE (%)
PBTFB-C8 [(a)]	1:2	0.79	6.60	0.33	1.73
PBTFB-C8 [(a)]	1:3	0.78	7.52	0.35	2.08
PBTFB-C8 [(a)]	1:4	0.78	6.18	0.34	1.66
PBTFB-C2C6 [(a)]	1:3	0.90	5.73	0.35	1.80
PBTFB-C2C6 [(a)]	1:4	0.72	5.81	0.36	1.52
PBTFF-C8 [(a)]	1:1.75	0.85	5.23	0.37	1.62
PBTFF-C8 [(a)]	1:2	0.83	6.13	0.36	1.82
PBTFF-C8 [(a)]	1:2.25	0.82	5.28	0.33	1.42
PBTFF-C2C6 [(a)]	1:2	0.95	0.47	0.46	0.21
PBTFF-C2C6 [(b)]	1:3	0.80	4.51	0.32	1.17
PBTFF-C2C6 [(b,c)]	1:3	0.90	4.43	0.33	1.31

Table 3 Photovoltaic parameters for the polymers with different blend ratios. Devices with an active area of 0.28cm², tested under AM 1.5G irradiation at an intensity of 1000 W.m^{-2}. (a) deposited from a chlorobenzene solution, (b) Processing additive: 3% 1,8-diiodooctane, (c) Thermal annealing, 5 minutes at 80°C.

For **PBTFB-C8**, the best performance was obtained with a weight ratio polymer:[70]PCBM of 1:3. The PCE of 2.08% with a V_{OC} of 0.78 V, a FF of 0.35 and a Jsc of 7.52 mA.cm^{-2} was achieved. In order to explain the relatively high current density delivered by this cell, we measured the charge carriers mobility (μ) in real devices using the photo-CELIV (Charge Carrier Extraction by Linearly Increasing Voltage) technique (See ESI). The mobility of the charge carriers for the cell fabricated with 1:3 blend ratio was around 1.10^{-4} cm²/V/s whereas it decreased to 4.10^{-5} cm²/V/s when 1:4 blend ratio was used. This deterioration of the charge carriers mobility could explain that a lower J_{sc} and a lower PCE were observed for non optimized blends (see table 3).

For **PBTFB-C2,6** devices, despite of a higher Voc that reaches 0.90V, a lower PCE of 1.80% was obtained. This lower value originates from a lower J_{sc} related to a lower mobility of the charge carriers as it has already been demonstrated for polymers bearing branched alkylchains.[18c] For **PBTFF-C8** based devices the highest performances were obtained with a weight ratio of

1:2. The PCE of 1.82% with a slightly higher V_{OC} of 0.82 V, a lower Jsc of 6.13 mA.cm^{-2} and a FF of 0.36 was obtained. The devices based on **PBTFB-C2C6** show slightly lower performances compared to the devices containing the analog polymer with linear alkyl chains. Because of a deeper HOMO energy level position for this polymer, the devices demonstrate, as expected, a higher V_{OC} value of 0.9V. However the devices show a slightly lower J_{sc} of 5.73 mA.cm^{-2}, giving a PCE of 1.80%. Surprisingly the devices containing **PBTFF-C2C6** show a much lower PCE of 0.21% despite of a very high V_{OC} of 0.95V.The very low PCE is due to a dramatic drop of the current delivered by the cell. To understand the origin of this very low J_{sc}, the surface morphology of the bulk-heterojunction was investigated by AFM.

The Atomic Force Microscopy (AFM) images of the different blends are shown in Figure 3. Interestingly, we observed a totally different morphology for the blends fabricated with benzothiadiazole or fluorenone based copolymers. As pointed out in the AFM images, the relative solubility of **PBTFF-C2C6** to the [70]PCBM one had a significant impact on the final morphology of the active layer (see Figure 3d). The 100nm scale phase segregation in this blend is very likely responsible for the enhanced recombination of the charge carriers and the dramatic drop of the current density. Our attempts to improve the morphology of the donor-acceptor networks by thermal treatment were not successful. Therefore with the goal to enhance the miscibility of the two components and to favor the formation of a better interpenetrating donor-acceptor network, we decided to use 1,8-diiodooctane (DIO) as a processing additive.

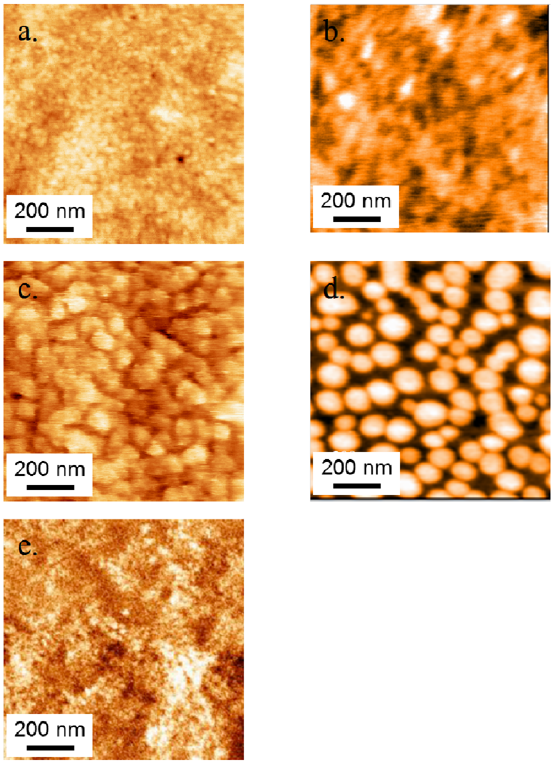


Figure 3: AFM images, topography, 1µm x 1µm of active layer made of: a) PBTFB-C8: $PC_{70}BM$ 1:3, b) PBTFB-C2C6: $PC_{70}BM$ 1:3, c) PBTFF-C8: $PC_{70}BM$ 1:2, d) PBTFF-C2C6: $PC_{70}BM$ 1:2, e) PBTFF-C2C6: $PC_{70}BM$ 1:2 (CB+3% DIO), thermal annealing, 5 minutes at 80°C.

DIO is known to selectively dissolve the fullerenes, and the use of this compound in small amount can increase the relative solubility of the fullerene compared to the polymer in the processing solution, and it ensures that the two materials are deposited at the same time during the spin-coating process.[23b,24] Since the optimized concentration of the processing additive depends strongly on the polymer solubility and the thin-film preparation process, several concentrations were tested. We found that the best morphology was achieved with a DIO concentration of 3% (in volume) (see Figure 3e).

The devices based on the **PBTFF-C2C6**/[70]PCBM blends and processed with these conditions showed as expected a much better performance with a power conversion efficiency of 1.17%. This strong improvement can be directly correlated to the 10 times enhanced current density delivered by the cell. In this particular case we found that a thermal treatment at 80°C for a short period helps improving the PCE up to 1.31%. The same strategy was then applied for the fabrication of the solar cells with the other polymers, leading in all cases to a deterioration of the performances of the solar cells.

Finally, Incident-Photon-to-Current-Efficiency (IPCE) experiments were carried out with the best performing cells. The results confirmed that the ICT absorption bands of the polymers contribute predominantly to the generation of the current with efficiency close to 40% for the benzothiadiazole based copolymer. Interestingly, we show that despite of a lower intensity of the ICT absorption band, the fluorenone-containing materials show efficiency close to 30% in the visible.

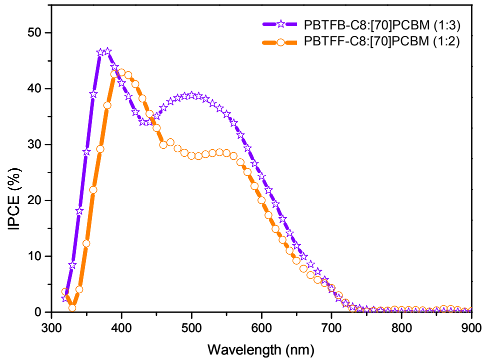


Figure 4: IPCE curve of the best performing photovoltaic cells fabricated with **PBTFB** or **PBTFF** copolymers.

Conclusions

We have synthesized and rationnaly compared the optoelectronic and photovoltaic properties of a series of p-type alternating copolymers based on oligothiophene-fluorene electron-donating units, and fluorenone or benzothiadiazole electron-withdrawing units. The polymers were synthesized by Suzuki reactions and it was found that the choice of the solvent for the polymerization reaction is crucial to achieve high molecular weight polymers and it strongly depends on the type of electron withdrawing unit. We demonstrated that the copolymers containing branched alkyl chains as solubilising groups show a higher oxidation potential when studied in their solid state, resulting in a deeper HOMO energy level. All the polymers show a high band gap. We highlight in this work the crucial role of the side solubilizing groups attached to the polymer backbones that have a significant impact on the morphology of the blends and the solar cells power conversion efficiency. Devices based on fluorenone-copolymers and [70]PCBM blends showed a Voc of up to 0.95V (for the ramified alkyl chain based polymer) and power conversion efficiencies up to 1.82% (for the linear alkyl chain based polymer) under AM1.5 simulated sunlight (1000 W.m^{-2}) conditions whereas the ones based on benzothiadiazole-copolymers showed a slightly lower Voc of 0.90V but higher power conversion efficiencies up to 2.08% for devices with a device area of 0.28cm². The performances obtained with these fluorenone-based copolymers are the highest one reported for this class of materials. Based on these results, future developments will be focused on the synthesis of alternating copolymers employing electron-withdrawing units substituted by linear alkyl-chains and the development of new polymerization methods in order to improve their macromolecular parameters and the performances of the solar cells employing them.

Experimental

Materials

Reagents and chemicals were purchased from Aldrich, TCI or Kaironkem and used as received, except for THF which was distilled over sodium-benzophenone prior to use. Thin layer chromatography was performed on silica gel-coated aluminium plates with a particle size of 2-25 µm and a pore size of 60 Å. Merck 60 (70-230 mesh) silica was used for flash chromatography. All synthesised products were identified by ^{1}H and ^{13}C NMR spectroscopy, as well as by elemental analysis or HRMS. NMR spectra were recorded in chloroform-d, containing tetramethylsilane (TMS) as internal standard, on a Bruker AC200 spectrometer or Bruker AC400. Elemental analyses (C, H, N, and S) were carried out by by CRMPO at the university of Rennes 1 (France). 2,7-bis(5'-bromo-4-octyl-5,2'-bithien-2-yl)-fluorenone (BTF8-Br2) was synthesized according to already reported procedure[17].

General polymerisation procedure for PTFB8 and PTFF8. (BTB8-Br2) or (BTF8-Br2) (1eq. 0.47mmol), and 2,2'-(9,9-dihexyl-9H-fluorene-2,7-diyl)-bis(5,5-dimethyl-1,3,2-dioxaborinane) (1eq, 0.47mmol) were charged in a 25 ml flask and purged under N$_2$. After adding toluene (6 ml) the mixture was degassed and followed by the addition of Na$_2$CO$_3$ solution (2 mL, 2.0 M), and the catalysts Pd$_2$(dba)$_3$ (8.6 mg, 9 10^{-3} mmol) and P(o-tolyl)$_3$ (17 mg, 5.4 x 10^{-2} mmol). The mixture was then heated at 120 °C for 72 h. For end-capping, 2-thiophene boronic ester (185 mg, 0.94 mmol) and 2-bromothiophene (154 mg, 0.94 mmol) were added and the mixture was heated for another 2 h. After cooling to room temperature, the mixture was poured into methanol. The precipitate was collected and washed with methanol vigorously then extracted by soxhlet extraction with acetone and chloroform.

Poly [4-(5'-(9,9-dihexyl-7-(3'-octyl-2,2'-bithiophen-5-yl)-9H-fluoren-2-yl)-3-octyl-2,2'-bithiophen-5-yl)benzo[c][1,2,5]thia dia zole] (PTFB-C8). (375 mg, 67 %) Mn = 5.64 kDa (eq. PS); Mw = 8.61 kDa (eq. PS); PDI = 1.56. ^{1}H NMR (200 MHz, CDCl$_3$, δ): 7.95 (s, 2H), 7.81 (s, 2H), , 7.05 (d, J = 3.8 Hz, 2H), 6.97 (d, J =3.8 Hz, 2H), 2.79 (t, J= 7.8 Hz, 4H; CH$_2$), 1.78-1.64 (m, 4H; CH$_2$), 1.21 (m, 20H; CH$_2$), 0.89 (t, 6H, J = 6.6 Hz; CH$_3$).^{13}C NMR (200 MHz, CDCl$_3$, δ): 152.97, 152.22, 145.46, 145.33, 140.93, 137.25, 135.75, 133.38, 133.10, 131.16, 127.29, 125.80, 125.59, 120.17, 78.10, 77.46, 76.83, 55.79, 40.90, 32.39, 30.16, 29.96, 29.82, 23.17, 23.06, 14.62, 14.50.

Poly[2-(5'-(9,9-dihexyl-7-(3'-octyl-2,2'-bithiophen-5-yl)-9H-fluoren-2-yl)-3-octyl-2,2'-bithiophen-5-yl)-9H-fluoren-9-one] (PTFF-C8) (starting from 200mg of BTFF8-Br2: 92 mg, 33 %); Mn = 3.24 kDa (eq. PS); Mw = 4.96 kDa (eq PS); PDI = 1.53. ^{1}H NMR (200 MHz, CDCl$_3$, δ): 7.83-6.86 (m, 16H), 2.80 (br, 4H), 2.01 (br, 4H), 1.68-1.07 (br, 40H), 0.89 (br, 6H), 0.76 (br,6H). ^{13}C NMR (200 MHz, CDCl$_3$, δ): 151.14, 150.45, 146.66, 142.42, 140.47, 137.99, 134.60, 134.55, 134.35, 130.71, 129.83, 129.15, 126.33, 126.25, 124.16, 120.61, 120.41, 120.37, 119.30, 119.24, 89.45, 77.23, 76.60, 75.96, 40.02, 31.53, 31.50, 31.08, 30.14, 29.30, 29.26, 23.33, 22.30, 22.18, 13.76.

poly(4-(5'-(9,9-bis(2-ethylhexyl)-9H-fluoren-2-yl)-3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-7-(3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole) (PBTFB-C2C6) 200 mg (0.236 mmol) of 4,7-bis(5'-bromo-3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole (BTB-C2C6) and 0.496 mL of 0.5M (0.248 mmol) solution in toluene of 9,9-Di(2-ethylhexyl)fluorene-2,7-diboronic acid bis(1,3-propanediol)ester are solubilized in 12 mL of solvant (toluene only). The solution is degassed by 4 consecutive freeze-pump-thaw cycles before filling tube with Argon. 0.496 mL of 1M aqueous solution of K$_2$CO$_3$, 2 drop of Aliquat 336 and finally 10.9 mg of Pd(PPh$_3$)$_4$ are added to the solution. The tube is put in a pre-heated oil bath at 100°C during 42 hours. 34 mg of para-methoxybenzene boronic acid is added and after 1h30, 80 mg of iodoanisole. After 1h30, the solution is cooled down. Products are precipitated in methanol and the polymer is purified by soxhlet extraction using acetone and finally chloroform. 174 mg of very dark red powder is obtained (67% yield). RMN ^{1}H (CDCl$_3$, 200MHz): δ= 8.01 (s, 2H), 7.86 (d, 2H), 7.74-7.61 (m, 6H), 7.35 (d, 2H, J=3.4 Hz), 7.25 (s, 2H), 2.88 (d, 4H, J=6.3 Hz), 2.13-2.04 (m, 4H), 1.88-1.80 (m, 2H), 1.47-1.25 (m, 18H), 0.97-0.55 (m, 40H).

Poly(2-(5'-(9,9-bis(2-ethylhexyl)-9H-fluoren-2-yl)-3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-7-(3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-9H-fluoren-9-one) (PBTFF-C2C6)

100 mg (0.112 mmol) of 2,7-bis(5'-bromo-3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-9H-fluoren-9-one (BTF-C2C6) and 0.235 mL of 0.5M (0.117 mmol) solution in toluene of 9,9-Di(2-ethylhexyl)fluorene-2,7-diboronic acid bis(1,3-propanediol)ester are solubilized in 8 mL of solvant (toluene only or toluene/DMF). The solution is degassed by 4 consecutive freeze-pump-thaw cycles before filling tube with Argon. 0.235 mL of 1M aqueous solution of K$_2$CO$_3$, 2 drop of Aliquat 336 and finally 5.2 mg of Pd(PPh$_3$)$_4$ are added to the solution. The tube is put in a pre-heated oil bath at 100°C during 42 hours. 34 mg of para-methoxybenzene boronic acid is added and after 1h30, 80 mg of iodoanisole. After 1h30, the solution is cooled down. Products are precipitated in methanol and the polymer is purified by soxhlet extraction using acetone and finally chloroform. 84 mg of very dark red powder is obtained (64% yield). RMN ^{1}H (CDCl$_3$,

200MHz): δ= 7.94 (s, 2H), 7.80-7.51 (m, 10H), 7.33 (d, 2H, J=3.4 Hz), 7.25 (s, 2H), 7.18 (d, 2H, J=3.4 Hz), 2.80 (d, 4H, J=6.3 Hz), 2.08-2.04 (m, 4H), 1.78-1.68 (m, 2H), 1.47-1.25 (m, 18H), 0.91-0.50 (m, 40H).

Physicochemical Characterizations

UV-vis absorption spectra were recorded in solution on a Perkin-Elmer Lambda 2 spectrometer (wavelength range: 180-820 nm; resolution: 2 nm) and were confirmed during the SEC analyses using a diode array UV-vis spectrometer. Electrochemical studies of the synthesized molecules were carried out in a one compartment, three-electrode electrochemical cell equipped with a flat platinum working electrode (7 mm^2), a Pt wire counter electrode, and a Ag wire pseudo-reference electrode, whose potential was checked using the Fc/Fc$^+$ couple as an an internal standard. The electrolyte consisted of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution in acetonitrile. The experiments were carried out in a glove box filled with argon.

Device fabrication and characterization

Bulk-heterojunction solar cells were fabricated on a glass substrate covered by a transparent conductive oxide, ITO, according to the procedure and layout described in ref. [16a]. The ITO was covered with a 40 nm thick interfacial PEDOT/PSS layer (Baytron-P), onto which the active layer was spin-coated from chlorobenzene solutions containing the donor/ PCBM mixture. Finally, a 20 nm thick layer of Ca was evaporated on top of the active layer and covered by the aluminium electrode (200 nm) or in some particular cases TiO_2 nanoparticules were spin coated from acetone solution before the evaporation of the top electrode. The active surface of the devices was 0.28 cm^2. Current–voltage, *I-V*, characteristics and PCEs of the solar cells, illuminated through the ITO, were measured in inert atmosphere via a computer controlled Keithley 1 SMU 2400 unit using 100 mW.cm^{-2} air-mass (1.5)-simulated white light generated by a Oriel SP94043A (Xe Lamp) Solar simulator. These simulated conditions are consistent with most published works to date. A monocrystalline silicon solar cell, calibrated at the Fraunhofer Institut Solare Energiesysteme (Freiburg, Germany), was used as a reference cell to confirm stabilization of the 100 mW.cm^{-2} illumination. The used apparatus was a standard system that is widely used and gives mismatch factors of around 4% in the 300 to 1100 nm range. The mismatch factors were obtained by comparison of simulated light with outdoor tests. The temperature of the polymer heterojunction, measured using a thermocouple (Pt100) mounted on the ITO substrate, reached 30°C during the first *I-V* characterization.

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Notes

[a] CEA-INAC-UMR5819-SPrAM (CEA/CNRS/UJF) 17, Rue des Martyrs, F-38054 Grenoble, France. E-mail: renaud.demadrille@cea.fr
[b] CEA, LITEN, Département des Technologies Solaires, INES, 50 avenue du Lac Léman, 73375 Le Bourget du Lac, France.

Contributions: N.D and W. Z. N. Y contributed equally to this work. ND and N.W.Z.Y performed the synthesis and the characterization of the materials and treated the data. N.L and S.B carried out the fabrication and the characterizations of the solar cells. J.F.V carried out the CELIV measurements. F.F and B.G performed the morphology study of the blends with AFM. J.P.T supervised the work, and R.D designed the materials and the experiments, contributed to the analysis of the data and wrote the paper. All the authors revised the manuscript.

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High Band Gap copolymers containing 2,1,3-benzothiadiazole or fluoren-9-one units were synthesized and compared for an application in bulk-heterojunction solar cells.