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Synthesis, characterization and device optimisation of new poly(benzo[1,2-*b*:4,5-*b'*]dithiophene-*alt*-thieno[3,4-*d*]thiazole) derivatives for solar cell applications.

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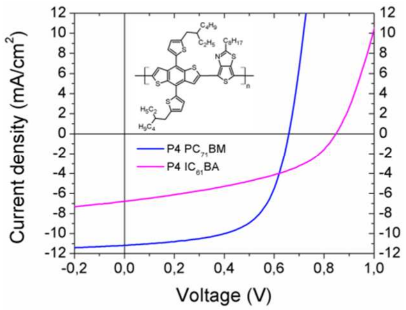
Abstract

New alternating copolymers based on benzo[1,2-*b*:4,5-*b*']dithiophene and thieno[3,4-*d*]thiazole derivatives have been synthesized by using different combinations of side chains and spacers in order to study their effect on the optical, electrochemical and photovoltaic properties. Optical and electrochemical characterization were performed and the resulting copolymers exhibit optical bandgaps ranging from 1.66 to 1.80 eV, HOMO energy levels between -5.19 and -5.30 eV and LUMO energy levels between -3.60 and -3.72 eV. Photovoltaic devices were fabricated and characterized after a careful optimization of the active layer fabrication by using different solvents, additives and acceptors. Following this process, PCEs up to 4.4 % were obtained.

TOC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Voltage (V)
12
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
-0,2
0,0
0,2
0,4
0,6
0,8
1,0
P4 PC$_{71}$BM
P4 IC$_{61}$BA
C$_4$H$_9$
C$_2$H$_5$
C$_8$H$_{17}$
N
S
n
H$_5$C$_2$
H$_9$C$_4$

Introduction

Although recent progress has been made into harvesting energy from the sun to efficiently produce electricity, there are still many challenges to overcome before having a reliable and cost-effective technology. In this regard, organic solar cells have attracted a lot of attention due to their easy processability, low cost of manufacturing and flexibility. Up to now, power conversion efficiencies (PCE) in excess of 10 %[1-3] for single junction solar cells, up to 10.8 %[4-8] for tandem solar cells and up to 11.8 %[9,10] for triple junction solar cells have been reported. A major part of this progress has been accomplished by the synthesis of new p-type conjugated polymers. Push-pull alternating copolymers have shown to be a convenient method to tune the HOMO-LUMO energy levels. Moreover, it is also possible to tune the acceptor used in the bulk heterojunction (BHJ) active layer to optimise the power conversion efficiency. [6,6]-phenyl C_{61} butyric acid methyl ester ($PC_{61}BM$) has been one of the first acceptor to be utilized to obtain good efficiencies. [6,6]-phenyl C_{71} butyric acid methyl ester ($PC_{71}BM$) has also been used to improve the absorption in the low wavelength region. More recently, other derivatives of fullerenes have started to be utilized in high efficiency solar cells. For instance, indene-C_{61} bisadduct ($IC_{61}BA$) and indene-C_{71} bisadduct ($IC_{71}BA$) have shown to significantly increase the open circuit current in the photovoltaic devices. While the use of ICBA enhances the open circuit voltage (V_{oc}) in comparison to PCBM, very few examples have been reported where the PCE has been higher with ICBA than with PCBM.[11,12]

Along these lines, thieno[3,4-*d*]thiazole (TTz), a new electron-deficient unit for organic photovoltaic, has been used to synthesize new π-conjugated push-pull polymers. Copolymers based on benzo[1,2-*b*:4,5-*b*’]dithiophene (BDT) and TTz have demonstrated interesting photovoltaic properties with power conversion efficiencies up to 2.5%.[13,14] One may believe that these low PCEs were mainly due to the relatively high-lying HOMO energy level of the polymers which led to V_{oc} of about 0.6 V for these BDT-TTz derivatives. To address this problem, new copolymers based on TTz in combination with different electron-poor or electron-rich monomers were first synthesized. It was found that the tuning of the HOMO levels of TTz polymers by using different electron-poor or electron-rich units was somewhat inefficient.[15] In some cases, it has been possible to lower the HOMO energy levels but the physical properties (poor solubility and low molecular weights) of the resulting polymers were not compatible with photovoltaic applications. Since it was difficult to efficiently tune the HOMO energy levels of the TTz derivatives, new BDT-TTz derivatives with thiophene spacers and different alkyl chain combinations to optimize the solubility of the resulting polymers have been synthesized. This approach using thiophene spacers and different alkyl chains could vary the optical and electronic properties of the polymers and the morphology of the active layer.[16,17] Along these lines, and in order to increase the open-circuit voltage (V_{oc}), a BDT derivative bearing alkylthienyl side chains was used since there are known to decrease the HOMO energy level compared to the BDT with alkoxy side chains.[18-20] Finally, to increase the V_{oc} in the photovoltaic devices, a different acceptor ($IC_{61}BA$) was also used in the fabrication of the BHJ active layer. Herein, we report the synthesis of six polymers based on BDT and TTz derivatives and their photovoltaic properties.

Synthesis of the monomers

Two new TTz derivatives were designed as illustrated in Figure 1. One (compound **4**) with the central TTz moiety with a straight alkyl chain and flanked with two thiophene units bearing alkyl side chains to ensure good solubility and another one (compound **6**) with the central TTz moiety with a branched alkyl chain flanked with two unsubsituted thiophene units. The branched alkyl chain on the TTz moiety was placed to ensure good solubility of the resulting copolymer. The synthesis of 4,6-dibromo-2-octylthieno[3,4-*d*]thiazole **(1)** and 2-(pentadecan-7-yl)thieno[3,4-*d*]thiazole **(2)** was done accordingly to the existing literature.[15,21] Stille couplings between compound **1** and 1-(trimethylstannyle)-2-octylthiophene gave compound **3** and was subsequently brominated with NBS to give the desired compound **4**. Compound **6** was obtained by the same general procedure from a Stille coupling of compound **2** with 2-(tributylstannyl)thiophene to afford compound **5**, which was also brominated with NBS. The detailed procedures are described in the Supporting Information (SI). It should be noted that relatively low yields obtained for compounds **3**-**6** is mainly due to difficult purification processes.

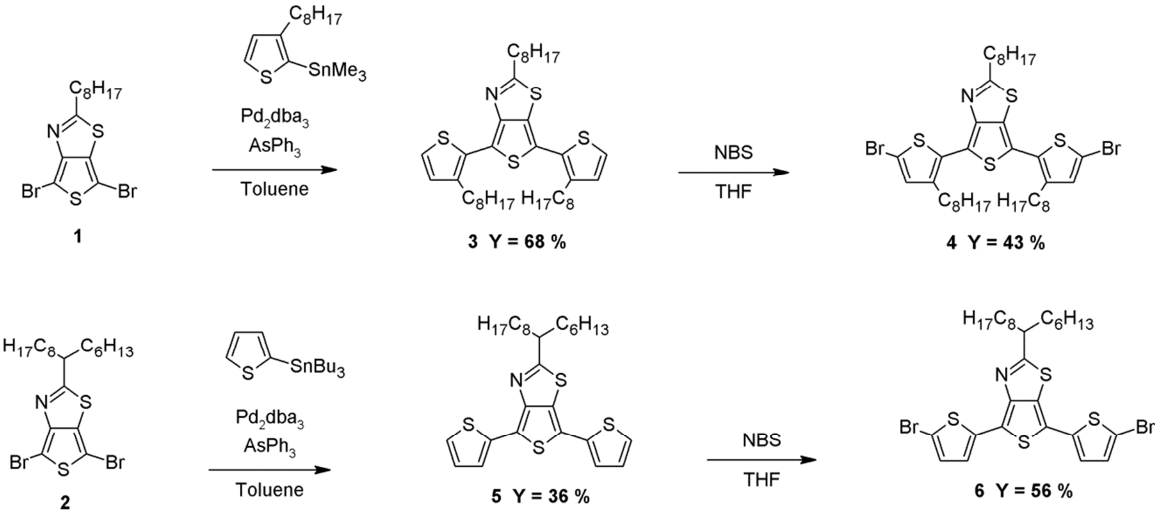

Figure 1 : Synthesis of thieno[3,4-*d*]thiazole derivatives.

Synthesis of the polymers

Six polymers have been synthesized by combining either 2,6-bis(trimethyltin)-4,8-di(ethylhexyl-oxyl)benzo[1,2-*b*:4,5-*b*']dithiophene **(7)** or 2,6-bis(trimethyltin)-4,8-bis(2'-ethylhexylthiophene)benzo[1,2-*b*:4,5-*b*']dithiophene **(8)** with compound **1**, **4** or **6**. The polymerizations have been conducted under Stille coupling conditions. Equimolar ratio of both monomers, 2% of Pd_2dba_3 and 8% of triphenylarsine ($AsPh_3$) were combined in dried and oxygen-free toluene. All polymers have been characterized by size-exclusion chromatography (SEC) based on monodisperse polystyrene standards in trichlorobenzene at 110 °C. The number-average molecular weight values obtained by SEC measurements for **P1** to **P6** vary between 14 and 32 kg/mol. Synthetic pathways are shown in Figure 2 and detailed in the SI while all the molecular weights are available in Table 1.

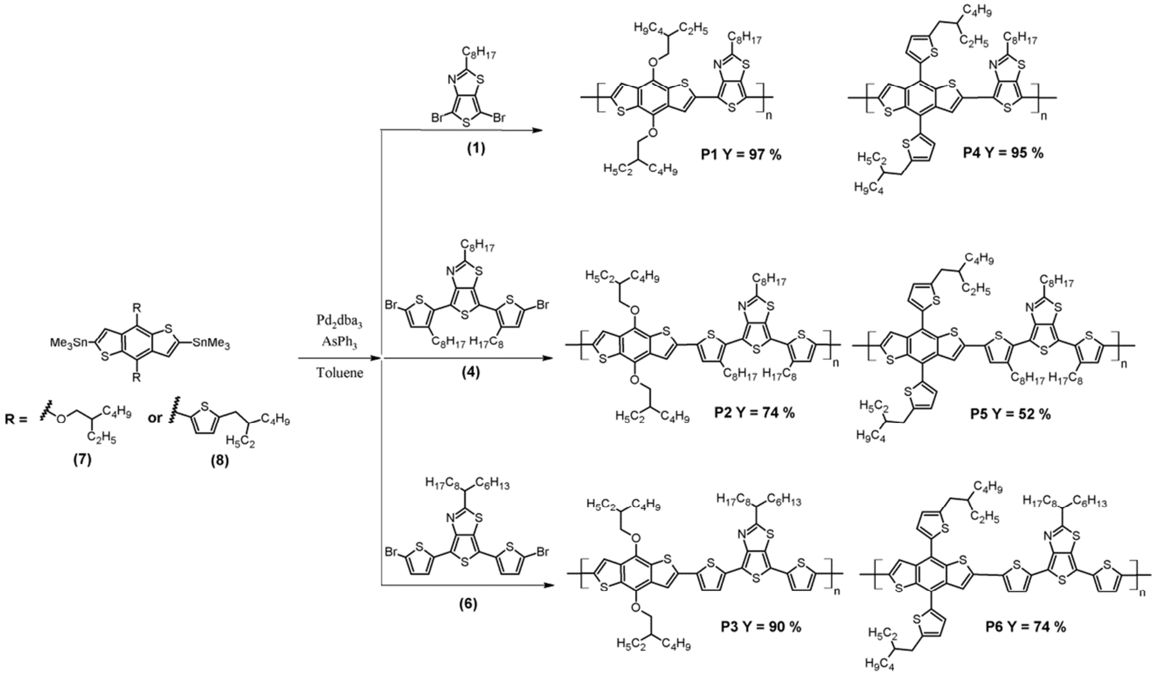

Figure 2: Synthesis of the polymers.

Optical and electrochemical properties

Solid-state UV-vis absorption spectra and cyclic voltammograms of polymers **P1** to **P6** are shown in Figures 3 and 4. Individual UV-vis spectra and voltammograms are reported in the Supporting Information. The solid-state UV-vis absorption spectrum of **P1** shows two absorption peaks at 578 nm and 630 nm with an estimated bandgap of 1.83 eV while cyclic voltammetry exhibits HOMO and LUMO energy levels of -5.30 eV and -3.60 eV respectively. **P2** exhibits absorption peaks at 564 nm and 610 nm with an estimated bandgap of 1.83 eV with HOMO and LUMO energy level of -5.22 eV and -3.65 eV. In the case of **P3**, the solid-state UV-vis spectrum shows also two absorption peaks at 568 nm and 612 nm with an optical bandgap of 1.80 eV. Cyclic voltammetry of **P3** exhibits a HOMO energy level of -5.24 eV and a LUMO energy level of -3.72 eV.

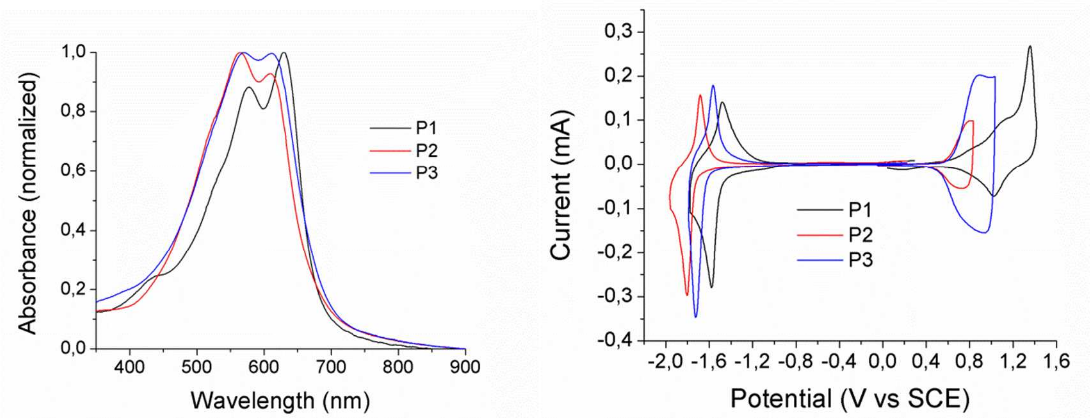

Figure 3: Solid-state UV-vis absorption spectra and cyclic voltammograms of **P1** to **P3**.

P4 displays a solid-state UV-vis absorption spectrum with two absorption peaks at 605 nm and 655 nm with an estimated bandgap of 1.72 eV while while cyclic voltammetry reveals HOMO and LUMO energy levels of -5.23 eV and -3.69 eV, respectively. **P5** shows an absorption peak at 572 nm with an estimated bandgap of 1.77 eV with HOMO and LUMO energy levels of -5.19 eV and -3.66 eV. In the case of **P6**, the spectrum shows also two absorption peaks at 585 nm and 631 nm with an optical bandgap of 1.76 eV. Cyclic voltammetry of **P6** shows a HOMO energy level of -5.24 eV and a LUMO energy level of -3.63 eV. Based on the solid-state UV-vis absorption spectrum, it seems that the addition of thiophene spacers on the **TTz** moiety has very little or no effect on the optical properties of the resulting polymers. In addition, based on the spectroscopic measurements, it seems that the utilization of two different **BDT** derivatives does not have a significant effect on the optical properties of the polymers. On the other hand, electrochemical characterizations seem to show that the utilization of a **BDT** unit with thiophene side chains increases the HOMO energy level of the resulting copolymer compared to the **BDT** with alkoxy side chains which is unexpected considering the existing literature[19]. In fact, according to that literature, the utilization of the thiophene side chains instead of the alkoxy side chains should slightly decrease the HOMO energy level. In our case, these contradictory results could be explained by the difficulty to precisely determine the HOMO energy level by solid-state cyclic voltammetry. Optical bandgaps, electrochemical bandgaps and HOMO and LUMO energy levels are summarized in Table 1.

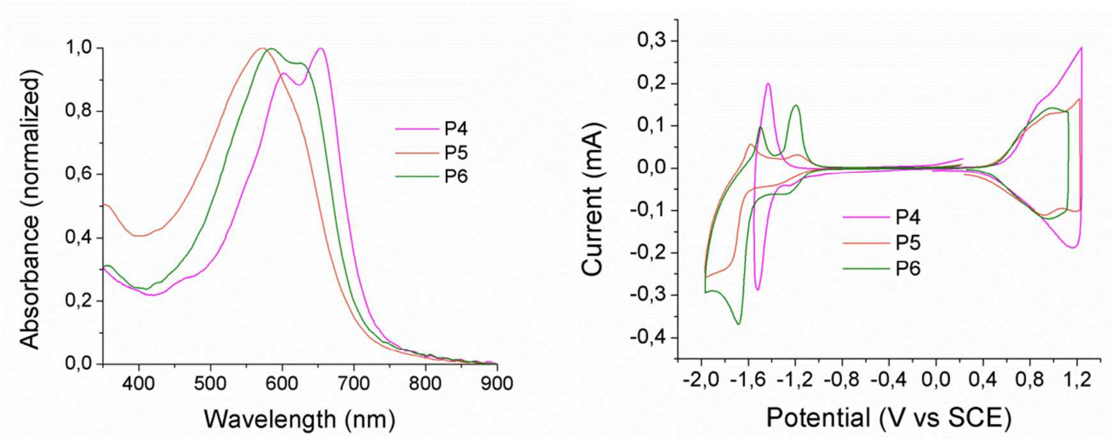

Figure 4: Solid-state UV-vis absorption spectra and cyclic voltammograms of **P4** to **P6**.

Table 1: Number-average molecular weight (M_n), weight-average molecular weight (M_w), polydispersity index (PDI), degradation temperature (T_d), and optical and electrochemical properties of **P1** to **P6**.

Polymer	M_n (kg/mol)	PDI	T_d (^oC)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{elec} (eV)	E_g^{opt} (eV)
P1	32	2.8	350	-5.30	-3.60	1.70	1.83
P2	14	1.5	340	-5.22	-3.65	1.57	1.83
P3	30	1.8	335	-5.24	-3.72	1.52	1.80
P4	23	1.4	450	-5.23	-3.69	1.54	1.72
P5	17	1.6	430	-5.19	-3.66	1.53	1.77
P6	20	1.8	440	-5.24	-3.63	1.61	1.76

Photovoltaic Properties

The six polymers have been studied in blends with $PC_{71}BM$ and $IC_{61}BA$ and used as photoactive layers in photovoltaic devices using a classical configuration consisting of an indium-tin oxide/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) transparent electrode and an LiF/Al reflective electrode with the active layer sandwiched in between. Each polymer has been optimized by studying the donor-acceptor ratio, the processing solvent, the use of additive and the layer thickness. In this study, $IC_{61}BA$ has been used to increase the V_{oc} of the device due to its higher LUMO energy level. However, the use of $IC_{61}BA$ has also been reported to have some drawbacks like the fact that the V_{oc} increase is often accompanied by a decrease of the photocurrent. One factor for the photocurrent loss is the lower absorption of the $IC_{61}BA$ comparatively to the $PC_{71}BM$, but it has also been shown that the use of fullerene multiadducts leads to a loss in charge generation efficiency and to a reduced charge carrier collection efficiency.[22] In this study, in some cases, the V_{oc} gain is enough to counterbalance the photocurrent losses but, in other cases, the photocurrent loss is too important to be compensated by the increased V_{oc}. The optimized processing conditions and photovoltaic performance of the six polymers for each acceptor used ($PC_{71}BM$ or $IC_{61}BA$) are shown in Table 2. *J-V* curves and EQE measurement of **P4** are shown in Figure 5. The other *J-V* curves and EQE measurements can be found in the supporting information. Generally, blends were made of a 1:2 ratio of polymer:acceptor mixed in chloroform unless otherwise indicated.

After optimization, **P1** shows best results when blended with $IC_{61}BA$ and 2% of 1,8-diiodooctane (DIO). Compared to the results obtained in the same conditions with $PC_{71}BM$, we observed an increase of the V_{oc} (0.54 V to 0.77 V) and FF (0.54 to 0.56) and a decrease of the J_{SC} from 9.74 mA/cm^2 to 7.27 mA/cm^2, for an overall PCE of 3.1 % instead of 2.7 % with $PC_{71}BM$. In the case of **P2**, the use of $PC_{71}BM$ or $IC_{61}BA$ led to very similar results after optimization. Even with the significant V_{oc} gain of 0.58 V to 0.74 V when using $IC_{61}BA$, the loss in photocurrent and fill factor led to optimized PCE of 1.8 % with $PC_{71}BM$ and 1.8 % with ICBA. For polymer **P3**, once again, the use of $IC_{61}BA$ led to a significant increase of the V_{oc} from 0.47 V to 0.73 V but also an increase of the FF from 0.53 to 0.56. These two gains were sufficient to counterbalance the J_{sc} loss from the use of $IC_{61}BA$ (9.79 mA/cm^2 to 6.84 mA/cm^2) to obtain a PCE of 2.8 % compared to 2.4 % with $PC_{71}BM$. For **P4**, the use of $PC_{71}BM$ has shown better results. After optimization, a J_{sc} of 10.96 mA/cm^2, a V_{oc} of 0.66 V and a FF of 0.61 for an overall PCE of 4.4 % were measured. While using $IC_{61}BA$, better V_{oc} of the order of 0.85 V accompanied by a very significant photocurrent loss to 6.28 mA/cm^2 leading to a much lower PCE of 2.3 % was obtained. It is also important to note that the results with $PC_{71}BM$ were obtained without the use of any additive. During the optimization, we observed that when the drying time of the active layer was increased by the use of an additive, the photocurrent and fill factor was significantly decreased leading to lower PCEs. The creation of non-optimal morphologies while using an additive is probably the cause of the poor photovoltaic performances. With 10 % of *o*-dichlorobenzene (ODCB) as an additive, the

PCE dropped to 3.5 % and then to 1.6 % with the use of 2 % DIO as an additive. In the case of **P5**, better results were also obtained while using $PC_{71}BM$. Even with a low V_{oc} of 0.49 V, a PCE of 2.6 % was achieved. When blended with ICBA, **P5** showed an increased V_{oc} of 0.71 but, the photocurrent was almost reduced by 50 % with a J_{sc} of 5.43 mA/cm^2. For **P6**, the polymer also showed better results when blended with $PC_{71}BM$ with a PCE of 3.1 %. Once again, $IC_{61}BA$ led to an increase in the V_{oc} from 0.58 V to 0.74 V while the J_{sc} decreased from 9.90 mA/cm^2 to 7.06 mA/cm^2 for an overall lower PCE of 2.8 %. While looking back to all these results, it is possible to observe that the addition of thiophene spacers did not have a positive effect on the performance. Effectively, in both polymer series, **P1** to **P3** and **P4** to **P6**, the polymers without thiophene spacers, **P1** and **P4**, showed the best results. These results also revealed that better performances are obtained with polymers based on the **TTz** unit having thiophene spacers without alkyl chains. In addition, when one compares polymers having the same **TTz** unit but copolymerized with the two different **BDT**, results shows that the **BDT** unit with thiophene side-chain exhibit, in all cases, a better performance. It is also interesting to point out that the use of the **BDT** with thiophene side-chain led to a significant increase of the V_{oc} for **P4** vs **P1** and for **P6** vs **P3** and a significant decrease for **P5** vs **P2**. While the polymer structures are very similar, it seems that a subtle change in their structure can lead to different electronic behaviors.

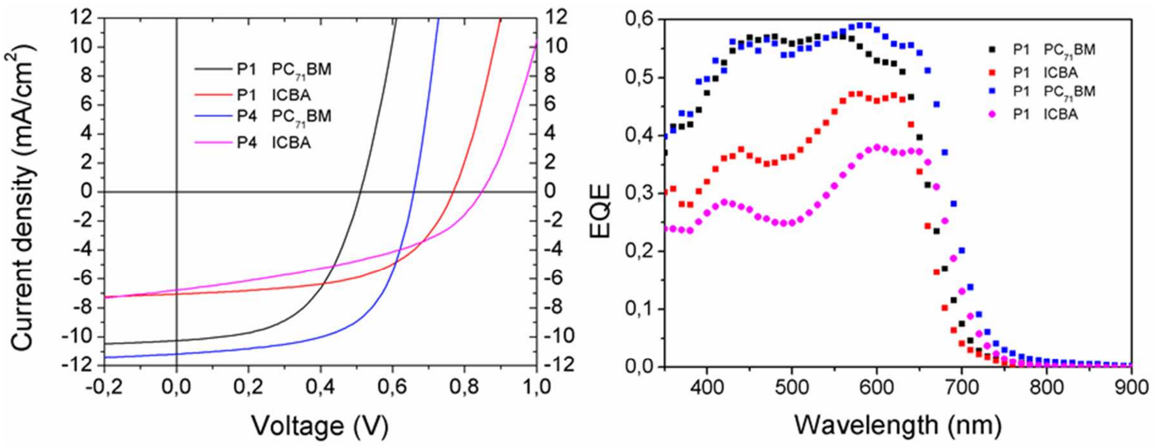

Figure 5 : *J-V* characteristics and EQE spectra of **P1** and **P4** for optimized devices using PC$_{71}$BM and IC$_{61}$BA.

Table 2: Optimized processing conditions and photovoltaic performance of **P1** to **P6**.

Polymer	Acceptor	Additive	d (nm)	J$_{sc}$^{a} (mA/cm^2)	V$_{oc}$ (V)	FF	PCE^a (%)
P1	PC$_{71}$BM	2% DIO	85	9.74	0.54	0.54	2.7
P1	IC$_{61}$BA	2% DIO	95	7.27	0.77	0.56	3.1
P2	PC$_{71}$BM	-	90	5.47	0.58	0.57	1.8
P2	IC$_{61}$BA	2% DIO	80	4.47	0.74	0.55	1.8
P3	PC$_{71}$BM	2% DIO	90	9.76	0.47	0.53	2.4
P3	IC$_{61}$BA	2% DIO	80	6.84	0.73	0.56	2.8
P4	PC$_{71}$BM	-	85	10.96	0.66	0.61	4.4
P4^b	IC$_{61}$BA	-	95	6.28	0.85	0.43	2.3
P5	PC$_{71}$BM	2% DIO	100	10.01	0.49	0.54	2.6
P5^b	IC$_{61}$BA	2% DIO	90	5.43	0.71	0.44	1.7
P6	PC$_{71}$BM	-	90	9.90	0.58	0.53	3.1
P6	IC$_{61}$BA	2% DIO	85	7.06	0.74	0.53	2.8

[a] J$_{sc}$ was calculated by integrating the EQE spectrum with the AM1.5G spectrum. [b] Blend was made with chlorobenzene instead of chloroform.

Conclusion

Six **BDT-TTz** polymers were synthesized and incorporated into solution-processed solar cells with $PC_{71}BM$ or $IC_{61}BA$ to give PCE up to 4.4%. The polymers possess fairly similar optical and electrochemical properties. The incorporation of thiophene spacers on the **TTz** moiety does not have a significant effect on the optical properties of the polymers. In contrary, the utilization of two different **BDT** derivatives seems to have some influence on the polymer properties. Two different acceptors, $PC_{71}BM$ and $IC_{61}BA$, were also used in the fabrication of the blends. After a careful optimization of the processing solvent and additives with both acceptors, we have been able to obtain PCEs ranging between 1.7 % and 4.4 %. $IC_{61}BA$ has been a helpful candidate to increase the open circuit voltage (V_{oc}) of the device but, in some cases, this gain was not sufficient to counter the photocurrent loss generated by its utilisation instead of $PC_{71}BM$. Finally, after reviewing the results, the incorporation of thiophene spacers into the polymer moiety does not improve the device performances.

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