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Sustainable Conjugated Polymer Synthesis in OPV: A Case Study from Conventional to Flow and Microwave-Assisted Synthesis [†]

Francesca Villafiorita-Monteleone [1,*], Benedetta Maria Squeo [1], Federico Turco [2], Antonella Caterina Boccia [1], Alberto Giacometti Schieroni [1], Daniele Piovani [1], Mariacecilia Pasini [1] and Stefania Zappia [1,*]

[1] Institute of Chemical Sciences and Technologies "G. Natta" (SCITEC), National Research Council (CNR), via A. Corti 12, 20133 Milan, Italy; benedetta.squeo@scitec.cnr.it (B.M.S.); antonella.boccia@scitec.cnr.it (A.C.B.); alberto.giacometti@scitec.cnr.it (A.G.S.); daniele.piovani@scitec.cnr.it (D.P.); mariacecilia.pasini@scitec.cnr.it (M.P.)
[2] Department of Chemistry, University of Milan, Via Golgi 19, 20133 Milan, Italy; federico.turco@unimi.it
* Correspondence: francesca.villafiorita@scitec.cnr.it (F.V.-M.); stefania.zappia@scitec.cnr.it (S.Z.)

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Abstract

Continuous flow synthesis and microwave-assisted synthesis represent two sustainable and efficient ways for the polymer production aligned with green chemistry principles, compared to conventional polymer synthesis. Here we present the case study of poly(4,4-dioctyldithieno(3,2-*b*:2′,3′-*d*)silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl (PSBTBT), a low band gap electron-donating polymer for organic photovoltaics (OPVs). The PSBTBT Stille cross-coupling polymerization conditions were optimized by comparing different synthetic methods: conventional, flow and microwave. To assess the impact of the different synthetic methods, detailed molecular and spectroscopic characterization, highlighting both the differences and similarities within the methodologies, was performed by several techniques, such as GPC, UV-Vis, PL, and NMR.

Keywords: conjugated polymers; low band gap polymers; Stille polycondensation; microwave assisted synthesis; continuous flow synthesis

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1. Introduction

The growing global energy demand, coupled with the urgent need to transition from fossil fuels to renewable energy sources, requires the development of innovative solutions for both energy generation and storage. Conjugated semiconducting materials have emerged as promising candidates due to their intrinsic advantages, including low production costs, lightweight nature, mechanical flexibility, and reduced environmental impact. Importantly, these features align well with the principles of circular chemistry and sustainable material design opening the way for the development of safe-by-design, eco-friendly optoelectronic devices [1].

A key challenge in the development of organic photovoltaics (OPVs) lies not only in improving performance and stability of the OPV devices but also in establishing environmentally friendly and scalable synthetic methods for conjugated polymers, which are essential components of the active layers [2]. Unfortunately, photoactive materials are usually produced only on a very small scale, both in research laboratories and industrial suppliers. This lack of a standardized and widely available materials supply leads to significant batch-to-batch variability, which in turn affects the active layer fabrication, and then the photovoltaic performance parameters [3–6]. Such inconsistencies substantially complicate both the comparison of results across different studies and the establishment of meaningful performance benchmarks [7].

The modern chemical industry is still developing new technologies to facilitate synthesis and scale-up processes, with the aim to scale up chemical production more sustainably and to reduce producing costs. Continuous flow and microwave-assisted methodologies represent two efficient and sustainable approaches aligned with the principles of green chemistry, enabling precise control over reaction conditions while reducing energy consumption and waste [8,9]. Together, these advanced synthetic methodologies represent key enablers for the greener and more cost-effective development of next-generation OPV materials.

Among emerging strategies, continuous flow chemistry approach involves the continuous pumping of reactants through a reactor, allowing for precise control over reaction parameters such as temperature, pressure, and residence time. This improves reproducibility, reduces reaction times, enhances safety, and significantly lowers solvent and energy consumption. Moreover, the scalability of flow chemistry simplifies the transition from laboratory to industrial-scale production. These advantages make continuous flow synthesis particularly attractive to produce conjugated polymers with well-defined properties, aligning with the principles of green chemistry and the growing demand for low-impact manufacturing technologies in the OPV field [8,10–13].

Likewise, microwave-assisted (MWA) synthesis has also emerged as a promising approach to sustainable polymer production [8]. The heating mode of MWA offers a good substitute for conventional heating, enabling rapid and uniform heating, and significantly decreases the reaction times and solvent usage, further contributing to energy efficiency and environmental compatibility. This improvement typically results from extreme temperatures in reactions carried out in closed containers under an autoclave condition and is frequently solely because of temperature effect [14]. Particularly, the use of microwave irradiation in polymer synthesis demonstrated comparable experimental results than those obtained using conventional thermal heating methods, with no detrimental effects on the resulting material performances [15–19].

Here we present the case study of poly(4,4-dioctyldithieno(3,2-*b*:2′,3′-*d*)silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl (PSBTBT), a low band gap electron-donating polymer [20].

We have developed the PSBTBT Stille cross-coupling polymerization using different approaches: conventional, continuous flow and microwave-assisted methods. To assess the impact of the different synthetic methods, we performed molecular and spectroscopic characterization to highlight correlations between the synthesis technique and the resulting material properties.

2. Materials and Methods

2.1. General Information for Synthesis

The two monomers, 4,4′-Bis(2-ethylhexyl)-5,5′-bis(trimethyltin)-dithieno[3,2-b:2,3-d]silole (DTS-EH-Sn) and 4,7-Dibromobenzo[c][1,2,5]thiadiazole (BT-Br_2), were commercially available. DTS-EH-Sn was purchased from Ossila BV and BT-Br_2 from Sigma-Aldrich (Saint Louis, MO, USA), respectively. Both were used as received without further purification. All other reagents were purchased from Sigma-Aldrich (Saint Louis, MO, USA). All the reactions were performed under dry nitrogen atmosphere. All the solvents have been deoxygenated and dried by standard methods before use; toluene was distilled on Na(s) and *N*,*N*-dimethylformamide (DMF) on Ca_2H, both under an inert N_2 atmosphere.

Synthesis of PSBTBT in batch reactor. The two monomers (2.5×10^{-2} mM) were dissolved in dry toluene in a dry, oxygen-free Schlenk tube. $Pd_2(dba)_3$ (7.5×10^{-4} mM) and $P(o\text{-tol})_3$ (4.5×10^{-3} mM) were then added to the mixture, which was stirred for 30 min at room temperature. The reaction mixture was subsequently placed in a pre-heated oil bath at 110 °C and stirred in the dark for 24 h prior to purification.

Synthesis of PSBTBT in flow reactor. The continuous flow experiments were conducted using a Vapourtec (Suffolk, UK) easy-Polymer E-Series system equipped with a perfluoroalkoxy (PFA) coiled tubular reactor (10 mL internal volume), and three peristaltic pumps. One pump delivered the reaction mixture, while the other two were used for the dilution of the crude solution leaving the reactor with toluene, and serving as a active back-pressure regulator. Idex fittings (IDEX Health & Science) were used with Tefzel® (EFTE) tubing (, ID: 1 mm). The reactants were introduced into the tubular reactor by pumping the reaction mixture from a nitrogen-filled Schlenk tube. The reactor coils were pre-heated to the desired temperature, and the flow rate was adjusted to achieve the required residence time (60 min). Prior to use, the system was purged with nitrogen and washed with dry toluene. Once ready, the valve was switched to allow the contents of the injection loops to enter the reactor coils.

The reaction mixture was prepared as follows: the two monomers were dissolved in dry toluene in a dry, oxygen-free Schlenk tube to achieve a final concentration of 2.5×10^{-2} mM for each. $Pd_2(dba)_3$ (7.5×10^{-4} mM) and $P(o\text{-tol})_3$ (4.5×10^{-3} mM) were then added to the mixture, and stirred for 30 min before injection.

Synthesis of PSBTBT in MW reactor. The microwave reactions were conducted using CEM Discover 2.0 (Charlotte, NC, USA). Reactions were carried out in nitrogen-filled 10 mL pressure vial from CEM designed for use with the Discover 2.0 system. The two monomers (2.5×10^{-2} mM), $Pd_2(dba)_3$ (7.5×10^{-4} mM) and $P(o\text{-tol})_3$ (4.5×10^{-3} mM) were added to a pressure vial and purged wth nitrogen. Dry solvent (4 mL total)was then added to the mixture, which was stirred for 30 min. The vials were subsequently sealed and placed in the the microwave reactor for 60 min. The reactions were conducted in "standard" mode, in which the system heats as rapidly as possible to the selected target temperature and then maintains that temperature for the specified reaction time. For the reactions carried out in toluene, the low dielectric loss tangent of the solvent prevented the temperature from reaching 160 °C under microwave irradiation.

General purification procedure. All crude products were subjected to the same purification procedure. In particular, the crude were diluted with toluene, cooled at r.t. and scavenger resin (3-mercaptopropyl-functionalized silica gel) was added and stirred overnight. Then, the reaction mixtures were filtered through Celite® to completely remove any trace of the metal catalyst washing with abbundant solvent [21]. The obtained mixture was concentrated under reduced pressure and precipitated in methanol. The blue solids were recovered and extracted using a Soxhlet apparatus, using sequentially acetone, hexane and chloroform. Further characterization was carried out on the chloroform extracts.

2.2. Structural and Molecular Characterizazions

Nuclear Magnetic Resonance (NMR). ^1H NMR spectra were recorded with a Bruker DRX 600 MHz spectrometer at 298 K. All chemical shifts were reported in parts per million (ppm) and calibrated on the residual signal of chloroform at 7.25 ppm. Commercial deuterated solvents were used as received.

Size Exclusion Chromatography (SEC). Molecular weight and molecular weight distribution (MWD) of the polymers were measured by high temperature size-exclusion chromatography (HT-SEC) using GPCV2000 system (Waters Corp., Milford, MA, USA) equipped on-line with a differential refractometer (DRI) as concentration detector and set of three Shodex HT (806M-805-804) columns (Showa Denko, Tokyo, Japan). The *o*-dichlorobenzene was used as the mobile phase. In order to avoid the thermal degradation and the formation of aggregates, the samples were prepared with an optimized procedure, as follows: (*i*) protection with butylated hydroxytoluene (BHT) antioxidant (0.05%); (*ii*) samples solubilization in oven at 140 °C for about one hour; (*iii*) filtration with sintered metal filters of 0.5 μm pores size; (*iv*) insertion of the samples in the injection compartment of the system at 135 °C. The prepared samples with concentrations of about 2 mg/mL were analyzed at 135 °C under a flow rate of 0.8 mL/min. Sixteen narrow MWD polystyrene standards with peak molecular weight ranging from $3.28 \cdot 10^6$ g/mol to 162 g/mol were used for calibration.

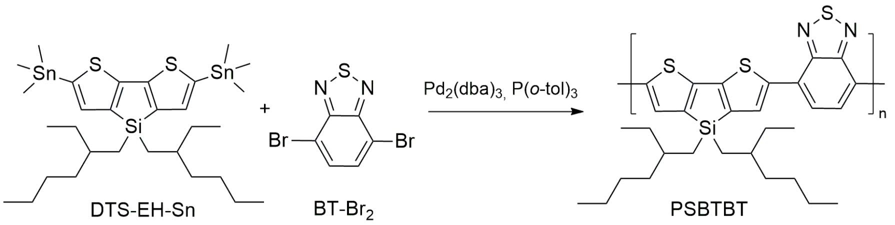
2.3. Photophysical Characterizations

UV-Vis Absorption Spectroscopy. UV–vis absorption spectra were recorded with a Lambda 900 spectrometer (Perkin-Elmer, Waltham, MA, USA). Optical characterizations were performed on the polymers dissolved in chloroform.

Photoluminescence (PL) Spectroscopy. PL spectra were obtained with NanoLog composed by an iH320 spectrograph equipped with a Synapse QExtra charge-coupled device, by exciting with a monochromate 450W Xe lamp. The spectra are corrected for the instrument response.

3. Results and Discussion

Poly(4,4-dioctyldithieno[3,2-*b*:2′,3′-*d*]silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl (PSBTBT) is a silole-containing, low band gap (LBG), electron-donating copolymer. It was extensively investigated due to its ability to absorb a broader portion of the solar spectrum, thereby contributing to higher power conversion efficiencies [22]. PSBTBT was selected as a model donor–acceptor alternating copolymer for testing different synthetic methodologies. In particular, Stille cross-coupling polymerization was carried out using both a continuous flow system and a microwave-assisted setup, in order to compare the properties of the resulting materials with those obtained using conventional batch methodology. The synthetic route investigated was reported in Scheme 1.



Scheme 1. Stille cross-coupling polymerization of PSBTBT investigated in this work.

The conventional batch polymerization, SZ173, was carried out under standard operating conditions, refluxing toluene for 24 h utilizing conventional heating in a dry environment.

Meanwhile, the optimization of the continuous flow polymerization was performed by varying the temperature and pressure parameters applied to a standardized reaction mixture. The reaction mixtures were prepared containing both monomers and the catalytic system maintaining fixed concentrations, as well as a defined residence time within the pre-heated coil reactor was tested, regulating the mixture volume and flow rate. To avoid the increase in the viscosity of the sorting crude solutions after flowing through the coil reactor, a convergent line supplying pure toluene for dilution 1:1 was used prior to collecting the solution in a flask containing toluene and metal scavengers, followed by the polymer purification process (Figure 1). As shown in Table 1, the increase in coil reactor temperature from 120 °C to 140 °C leads to remarkable increase in Mw values, from ≈6000 g/mol for sample SZ169 to ≈13,400 g/mol for sample SZ171, comparable with sample obtained in batch reaction. The Mw/Mn values of all samples prepared with flow conditions, ranging from 1.9 to 2.2, are comparable with the conventional batch product too (Table 1, Figure 2).

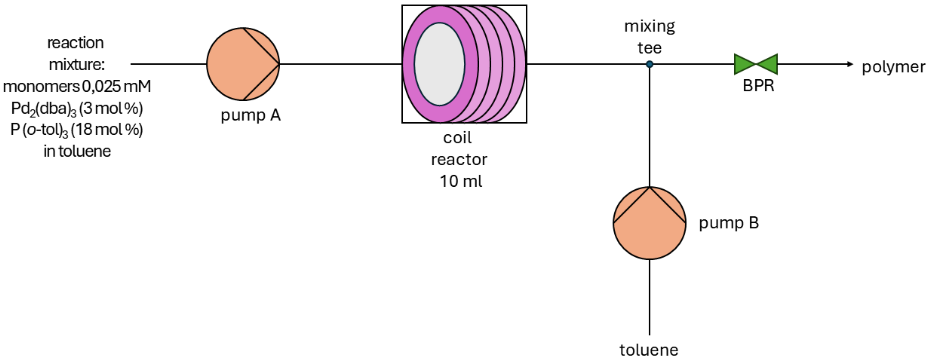


Figure 1. Sketched diagram of the flow polymerization system.

Table 1. Polymerization reaction conditions and molecular weight distributions (MWD) obtained for different methodologies. The analyses were carried out on the chloroform-soluble fractions.

Item	Method	Solvent	T [°C]	P [Bar]	Y [%]	Mn [g/mol]	Mw [g/mol]	Mw/Mn
SZ173	Batch [a]	Toluene	110	1	31	5656	11,119	1.97
SZ169	Flow [b]	Toluene	120	4	32	3156	6040	1.91
SZ170	Flow [b]	Toluene	120	6	37	3253	6485	1.99
SZ171	flow [b]	Toluene	140	4	27	6153	13,415	2.18
SZ172	flow [b]	Toluene	140	6	42	5544	10,849	1.96
FT110	MWA [b]	Toluene	140	1.7	32	4952	15,668	3.16
FT111	MWA [b]	DMF	160	1.2	54	5894	26,743	4.54
FT112	MWA [b]	DMF:toluene = 1:2	160	1.7	49	5367	11,072	2.06
FT113	MWA [b]	DMF:toluene = 1:10	160	2.3	55	6241	16,044	2.57

[a] reaction time 24 h; [b] reaction time 1 h.

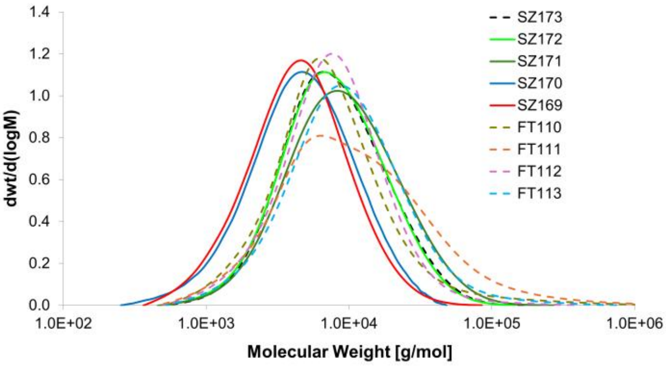


Figure 2. Comparison of differential molecular weight distribution of PSBTBT samples characterized through HT-SEC.

The MWA polymerization was carried out by charging the reactor vials under a nitrogen atmosphere with the reaction mixture dissolved in the selected solvent. During the optimization of the reaction conditions, various solvent mixtures were tested, including dry toluene, dry DMF, and two DMF:toluene mixtures at different volume ratios.

Pure toluene was included to allow a direct comparison with the other systems. However, due to its low dielectric constant and poor microwave absorption capacity, toluene proved ineffective in promoting efficient heating under microwave irradiation. To enhance heating efficiency, DMF was tested, which led to the growth of the polymeric chains. Unfortunately, the low solubility of PSBTBT in DMF caused precipitation of the polymer during the reaction, resulting in increased molecular weight and polydispersity of the product. Even if the Mw value increased both FT110 and FT111 samples, the increase in polydispersity to ≈4 is considered detrimental for the quality of the material.

Subsequently, two different DMF:toluene mixtures, 1:2 (FT112) and 1:10 (FT113), were evaluated in order to optimize the molecular properties of the resulting polymer. The products obtained were comparable with the batch SZ173 sample (Table 1, Figure 2).

For all samples, the reaction mixtures were quenched by dilution with toluene, and the same purification process was applied to isolate the chloroform-soluble fractions used in all subsequent characterizations.

All samples were characterized with high temperature-size exclusion chromatography (HT-SEC) to evaluate the molecular properties of the products obtained (Table 1, Figure 2).

The structural characterization of all products obtained with ^{1}H-NMR was performed. Figure 3 shows the aromatic region of the ^{1}H NMR spectra of the synthesized products. The resonances at 8.2 and 7.8 ppm were assigned to benzothiadiazole (electron acceptor moiety) and thiophene moieties (electron donating moiety), respectively.

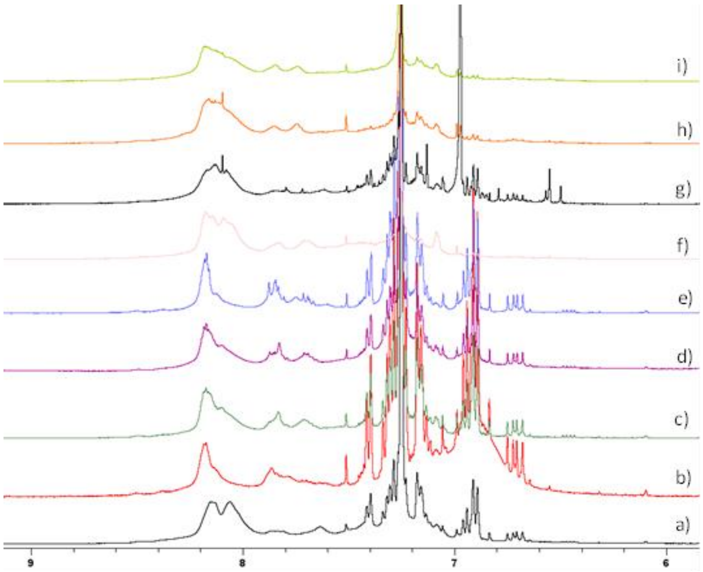
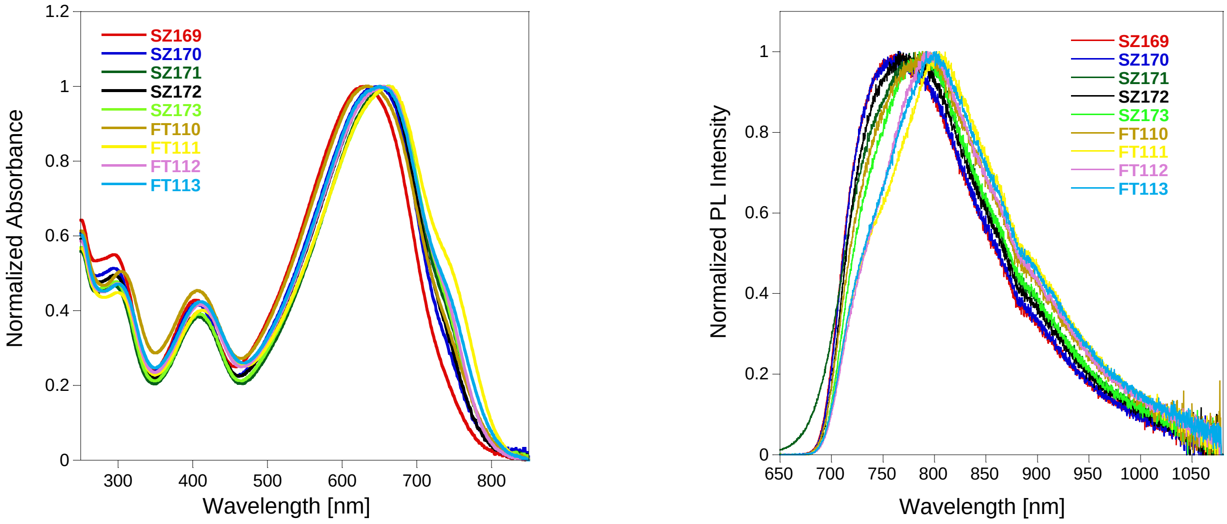


Figure 3. ^{1}H-NMR between 6 and 9 ppm. Proton spectra at 600 MHz and 298 K in $CDCl_3$ of: (a) SZ173; (b) SZ172; (c) SZ171; (d) SZ170; (e) SZ169; (f) FT110; (g) FT111; (h) FT112; (i) FT113 samples.

Figure 4 and Table 2 show the optical properties of all synthesized polymers in solution. All exhibit a large absorption band in the 500–750 nm range (Figure 4a), attributed to the free polymer chains. Nevertheless, the maximum absorbance drastically blue-shifts from 660 nm (SZ173) to a wavelength of ≈625 nm (SZ169). Furthermore, a low-energy shoulder appears at 750 nm in all polymers synthesized via microwave-assisted methods (FT110-113) (Table 2). This hypsochromic shift is probably due to different interchain interactions, related to increasing contact between the macromolecules, which in turn could cause a strong π-π stacking [23].



(**a**) (**b**)

Figure 4. Normalized (**a**) UV-Vis absorption and (**b**) PL spectra of all synthesized polymers in chloroform.

Table 2. Optical properties of all polymers in solution.

Polymer	λ_{abs}^{max}	λ_{em}^{max} *
SZ169	625	760
SZ170	643	760
SZ171	658	775
SZ172	653	760
SZ173	660	755
FT110	634	775
FT111	660	800
FT112	652	795
FT113	652	795

* λ_{exc} = 630 nm.

Similarly, the PL spectra (λ_{exc} = 630 nm) show a typical emission band in the 700–950 nm range, with blue or red-shifted maxima in relation to the different synthesis techniques (Figure 4b, Table 2).

4. Conclusions and Outlooks

Different advanced synthetic methodologies were tested to produce PSBTBT, a model low band gap electron donor polymer used in the active layer of organic photovoltaic (OPV) devices. The optimization of the polycondensation conditions led to the purification and characterization of samples with well-defined structural and optical properties, which will be the subject of in-depth investigation. The results obtained demonstrate that the proposed synthetic approach—namely, flow synthesis and microwave-assisted synthesis—enable the preparation of polymers with comparable molecular weight distributions and optical properties. In most cases, the yields are similar or even superior to those obtained via conventional methods, while significantly reducing reaction time. Indeed, the traditional thermal approach requires 24 h of heating, whereas both flow and microwave-assisted methods achieve comparable results in just 1 h, leading to substantial savings in both time and energy.

The next step will involve evaluating and comparing the residual palladium catalyst levels in the polymers, to determine whether their quantity varies depending on the synthesis technique employed, particularly with regard to covalently bonded palladium within the polymeric chains, which is known to be the main impurity affecting OPV efficiency. This analysis will be carried out using MALDI-TOF mass spectrometry. Furthermore, this characterization will provide insights into the concatenation of the polymer backbone. Specifically, structural defects along the backbone can interrupt π-conjugation, which leads to detrimental effects on device performance. To further assess the integrity of the polymer chains, 2D NMR spectroscopy will be conducted to identify potential concatenation errors in the polymer backbone structure.

Author Contributions: S.Z. and F.T. performed the synthesis of the materials; F.V.-M. was responsible for the optical characterization; A.C.B. was responsible for the NMR characterization; S.Z., A.G.S. and D.P. were responsible for the SEC characterization; S.Z., F.V.-M., B.M.S. and M.P. designed the experiments, discussed the data and prepared the manuscript. All authors have read and agreed to the published version of the manuscript.

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