Tetrahedron Letters xxx (xxxx) xxx



Contents lists available at ScienceDirect

Tetrahedron Letters



journal homepage: www.elsevier.com/locate/tetlet

Thiazolothiazole-based conjugated polymers for blade-coated organic solar cells processed from an environment-friendly solvent

Petr M. Kuznetsov^a, Sergey L. Nikitenko^a, Ilya E. Kuznetsov^a, Pavel I. Proshin^{a,b}, Daria V. Revina^c, Pavel A. Troshin^{d,a}, Alexander V. Akkuratov^{a,*}

^a Institute for Problems of Chemical Physics of the Russian Academy of Sciences (IPCP RAS), Academician Semenov Avenue 1, Chernogolovka 142432, Russian Federation ^b Dmitry Mendeleev University of Chemical Technology of Russia, Higher Chemical College of RAS, Miusskaya sq. 9, 125047 Moscow, Russian Federation ^c Moscow State University, Faculty of Fundamental Physical and Chemical Engineering, GSP-1, 1 Leninskiye Gory, 119991 Moscow, Russian Federation ^d Skolkovo Institute of Science and Technology, Bolshoy Boulevard 30, bld.1 Moscow, 121205, Russian Federation

ARTICLE INFO

Article history: Received 22 April 2020 Revised 6 May 2020 Accepted 11 May 2020 Available online xxxx

Keywords: Organic solar cells Photovoltaic modules Blade coating Thiazolothiazole Polycondensation

Introduction

In the last decade, rapid progress has been made in improving the performance of organic solar cells (OSCs). Recently, Chen and co-workers reported the champion tandem OSCs with power conversion efficiency (PCE) of 17.3% [1]. The achieved PCEs are already higher than that of multiple-junction inorganic solar cells based on amorphous silicon [2,3] and reached the threshold for the commercialization of OSCs. Nevertheless, some drawbacks of state-ofthe-art OSCs have impeded their large-scale production and application. In particular, record-high photovoltaic performances were achieved for laboratory OSCs of only 2-5 mm² in size, while increasing the device active area leads to a severe roll-off in their efficiency. Moreover, the active layers of high-efficiency solar cells are deposited predominantly using spin-coating techniques, which is not compatible with roll-to-roll production techniques [1,4,5]. Another challenge is related to the fact that the most efficient devices are fabricated using chlorinated organic solvents (chlorobenzene, dichlorobenzene, or chloroform), which are hazardous for the environment and toxic for humans, which limits their application for manufacturing of OSCs on industrial-scale

ABSTRACT

High efficiencies of organic solar cells (OSCs) are generally achieved for small-area devices processed from halogenated solvents, which are hazardous to human health and pollute the environment. Commercialization of OSCs requires the development of novel photovoltaic materials, which are suitable for large-scale fabrication of devices through printable techniques using environmentally-friendly solvents. In this work, we report the synthesis of two novel polymers comprising thiazolothiazole, benzothiadiazole (**P1**), and benzoxadiazole (**P2**) moieties and the fabrication of polymer-fullerene OSCs and photovoltaic modules by blade coating under ambient conditions. The **P1**-based solar cells and larger area modules showed tolerance to processing solvents and delivered encouraging efficiencies illustrating polymer **P1** as a promising material for environment friendly large-area photovoltaics.

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[6]. Thus, successful commercialization of OSCs requires the design and development of novel materials showing minimal efficiency roll-off upon upscaling and processable from non-toxic halogenfree solvents using roll-to-roll coating techniques suitable for mass production.

Thiazolo[5,4-*d*]thiazole-based (Tz) conjugated polymers have attracted significant attention in recent years as promising semiconductor materials for efficient and large-area OSCs [7]. Conjugated polymers with Tz units exhibit the tendency for strong π - π stacking in the solid state, which results in intense and broad absorption in the visible region as well as high charge carriers mobility [8–11]. Encouragingly PCEs > 10% were obtained recently for large-area devices demonstrating the high potential of Tz blocks for constructing efficient donor polymers [12].

In this work, we designed two novel Tz-based polymers with A-D-A moieties (A-acceptor and p-donor units) and explored them as absorber materials for OSCs and large-area photovoltaic modules. Both small-area solar cells and modules were fabricated using doctor blade coating from standard dichlorobenzene (DCB) and environment-friendly *m*-xylene solvents. The devices showed significant tolerance to processing solvents and upscaling while delivering encouraging efficiencies thus addressing the challenge of moving OSCs from research labs to industry.

* Corresponding author. *E-mail address:* akkuratow@yandex.ru (A.V. Akkuratov).

https://doi.org/10.1016/j.tetlet.2020.152037 0040-4039/© 2020 Elsevier Ltd. All rights reserved.

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Results and discussion

Conjugated polymers **P1** and **P2** were designed according to the "push-pull" concept with alternating donor (thiophene units) and acceptor blocks (benzothiadiazole or benzoxadiazole and Tz units). The synthesis of key monomers and polymers P1 and P2 is shown in Scheme 1. Condensation of aldehyde 1 [13] with dithiooxamide in N,N-dimethylformamide afforded 2,5-bis(3-(2-ethylhexyl)thiophen-2yl)-thiazolo[5,4-d]thiazole (2). Lithiation of compound 2 with *n*-butyllithium and further nucleophilic reaction of the dilithium intermediates with trimethylchlorostannane afforded the key monomer M1. Monomers M2 and M3 were synthesized in three steps. First, 5,6-bis(octyloxy)-2,1,3-benzothiadiazole [14] (3a) or 5,6-bis(octyloxy)-2,1,3-benzoxadiazole [15] (3b) were brominated with 2 equiv. of *N*-bromosuccinimide (NBS) in acetic acid. Further palladium-catalyzed Stille coupling of compounds 4a-b and 2,5-bis(trimethylstannyl)thiophene gave monomers M2 and M3. Conjugated polymers P1 and P2 were synthesized via Stille polycondensation reaction.

Polymers **P1** and **P2** were purified by Soxhlet extraction with hexane, acetone, dichloromethane, and chlorobenzene followed by concentration of the chlorobenzene fractions and precipitation of the polymers with ethanol. Both polymers **P1-P2** exhibit good solubility in common organic solvents such as chloroform, dichlorobenzene (DCB), tetralin, and xylenes. The molecular weight characteristics of **P1** and **P2** were estimated by gel permeation chromatography at 50 °C in chlorobenzene as eluent (Fig. S1) [16].

The weight average molecular weights (M_w) of 51 kDa and 78 kDa, with polydispersity indexes of 1.3 and 1.8 were obtained for **P1** and **P2**, respectively (Table 1).

The thermal properties of the polymers were investigated by thermal gravimetry analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere with a heating rate of 15 °C/min (Fig. S10a, ESI). The polymers showed high decomposition temperatures (T_d, corresponding to 5% weight loss) of 335 °C for **P1** and 320 °C for **P2** indicating good thermal stability for their application in OSCs. The differential scanning calorimetry (Fig. S10b, ESI) profile exhibits an endothermic peak of 278 °C and an exothermic peak of 244 °C corresponding to the melting (T_m) and solidification (T_c) temperatures of polymer **P1**, respectively. At the same time, no signals were recorded for polymer **P2**, thus indicating the less ordered structure of polymer **P2** in the solid state compared to polymer **P1**.

Optical properties of the polymers **P1** and **P2** were investigated in solution and in thin films. The normalized optical spectra are shown in Fig. 1 and the corresponding data are listed in Table 1.

Spectra of **P1** and **P2** in dichlorobenzene solutions show absorption maxima at 525 nm and 529 nm, respectively. A shoulder peak around 572 nm for polymer **P2** can be seen, which suggests the aggregation of polymer molecules in solution at room temperature. While going from solution to thin films, a strong bathochromic shift ($\Delta \lambda_{max} = 98-135$ nm) of the absorption maxima can be seen in the spectra of both polymers, thus indicating good supramolecular ordering of the polymer chains in the solid state. The optical bandgaps (E_{g}^{opt}) of 1.7 eV and 1.66 eV were estimated from the low energy band onset (λ_{edge}) in thin film spectra for polymers **P1** and **P2**, respectively (Table 1).

The electrochemical properties of polymer thin films were investigated using cyclic voltammetry as reported previously [16] (Fig. 1b). The oxidation onset potentials (E_{onset}^{ox}) of **P1** and **P2** were estimated as 0.52 V and 0.69 V, respectively. The HOMO energy



P2: R¹=2-ethylhexyl, R² =octyloxy, X=O 55 %

Scheme 1. Synthesis of conjugated polymers P1 and P2. Reagents and conditions: (i) dithiooxamide, DMF, reflux; (ii) BuLi, -60 °C, Me₃SnCl, RT; (iii) NBS, AcOH, 60 °C; (iv) 2,5-bis(trimethylstannyl)thiophene, Pd(PPh₃)₄ (0.002 equiv.), toluene, reflux.

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Table 1	
Physicochemical, optical, and electrochemical properties of polymers P1 and P2.	

	M _w , kDa	$M_{\rm w}/M_{\rm n}$	$\lambda_{\max}^{sol}/\lambda_{\max}^{film}/\lambda_{edge}^{film}$, nm	E_g^{opt} , eV	E_{onset}^{ox} ,V vs. Fc ⁺ /Fc	HOMO, eV ^a	LUMO, eV ^b	T _d , ℃	T_m/T_c , °C
P1	51	1.3	525/623/729	1.70	0.52	-5.62	-3.92	335	278/244
P2	78	1.8	529/664/745	1.66	0.69	-5.79	-4.13	320	n/a

^a HOMO energy was estimated from onset of the oxidation potential using Fermi energy of -5.1 eV for the Fc⁺/Fc redox couple.

^b LUMO level was estimated as E^{opt}_g + HOMO.



Fig. 1. Absorption spectra (a) and cyclic voltammograms of conjugated polymers P1 and P2 (b).

levels of the polymers were calculated from E_{onset}^{ox} potentials and using the value of -5.1 eV as the potential of the Fc⁺/Fc redox couple in the Fermi energy scale [17]. Conjugated polymer **P2** comprising benzoxadiazole acceptor blocks showed 0.17 eV lower HOMO energy compared to that of benzothiadiazole-containing **P1**. The observed effect can be related to the higher electronegativity of the oxygen atom [18,19]. Considering this fact, higher open-circuit voltages can be obtained for solar cells based on **P2** [20]. The LUMO energies were calculated based on HOMO energies and the optical bandgap of **P1** and **P2**.

Fig. 2 shows the energy levels diagram of the photovoltaic device components. The difference between HOMO and LUMO levels of the polymers and [70]PCBM ([6,6]-phenyl-C₇₁-butyric acid methyl ester) are greater than 0.3 eV, which is beneficial for exciton dissociation into free charge carriers [21].

We used standard bulk heterojunction organic solar cell configuration ITO/PEDOT:PSS (60 nm)/active layer (100-200 nm)/Mg (60 nm)/Al (50 nm). The active fullerene derivative ([70]PCBM) – conjugated polymer blend films were blade-coated in air from 1,2-dichlorobenzene as a standard solvent and from eco-friendly *m*-xylene. It is well known that the morphology of active layer films and consequently the photovoltaic performance of the OSCs can be improved by using additives with high-boiling points [22]. Therefore, screening of different compounds revealed diphenyl ether (DPE) as a promising processing additive for **P1(P2)**/[70] PCBM blends.

On the other hand, enhancing the performance of OSCs as well as their stability is closely related to interface engineering [23,24]. Therefore, we inserted polyhydroquinone [25] (PHQ) or fullerene derivative BLF-P [26] as interfacial buffer layers between the active layer and top electrode (Fig. 2b). These compounds were selected because their LUMO energy levels match the LUMO of the acceptor component [70]PCBM and the work function of the metal electrodes.

The parameters of devices fabricated under different conditions tested during optimization are shown in Table S1 (ESI). The photovoltaic characteristics of optimized solar cells are presented in Table 2. Current density–voltage (*J*-V) curves and external quantum efficiency spectra (EQE) measured under simulated AM1.5G illumination (100 mW cm⁻²) are shown in Fig. 3. Small-area OSCs based on polymer **P1** showed efficiencies of ~7%. When using dichlorobenzene as a solvent, the best performance was achieved by adding 1% of DPE and introducing a PHQ buffer layer, while xylene-processed OSCs showed the best characteristics without using any interfacial layers (Table S1, ESI). Both devices demonstrated high and comparable short-circuit current densities (*J*_{SC}), which match well with photocurrents obtained by integration of the corresponding EQE spectra.

As illustrated in Fig. 3 and Table 2, benzoxadiazole-containing polymer **P2** showed lower efficiencies in solar cells: 6.4% and 5.7% when processed from dichlorobenzene and xylene, respectively. Solar cells exhibited lower J_{SC} values and fill factors (FF) compared to that of **P1**-based devices that might be originating from poor charge transport or inappropriate morphology of the composite active layer [27]. Notably, OSCs with polymer **P2** displayed significantly enhanced V_{OC} that is in accordance with the low-lying HOMO energy of this donor polymer. It is worth noting that PHQ or BLF-P buffer layers did not improve the performance of **P2**-based solar cells (Table S1, ESI).

We investigated charge career mobilities for optimized polymer-fullerene blends using the space-charge limited current (SCLC) method [28]. The measurements were performed for the hole-only (ITO/PEDOT:PSS(60 nm)/blend/MoO₃(22 nm)/Ag (120 nm) and the electron-only (ITO/Yb(15 nm)/blend/Ca) devices. It was found that the optimized **P1**/[70]PCBM blends have higher and more balanced hole (μ_h) and electron (μ_e) mobilities than **P2**/[70]PCBM blends (Table 2). Thus, a more efficient charge transport in **P1**-based films can explain the higher J_{SC} and FF values achieved for devices.

In order to understand the morphology of **P1**/[70]PCBM and **P2**/ [70]PCBM blend films processed from DCB and *m*-xylene, atomic force microscopy (AFM) measurements were performed. AFM topography height images are shown in Fig. 4 and Figs. S11 and S12 (ESI).

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Fig. 2. Energy levels diagram for components of organic solar cells (a) and chemical structures of the used interfacial buffer layer materials PHQ and BLF-P (b).

Table 2	
Processing conditions and photovoltaic properties of optimized solar cells and modules based on P1/[70]PCBM and P2/[70]PCBM blee	nds.

	Area, cm ²	Conditions	V _{OC} , mV	$J_{\rm SC}~{\rm mA/cm^2}$	J ^{EQE} , mA/cm ²	FF, %	PCE, %	$\mu_h \ cm^2 V^{-1} s^{-1}$	$\mu_e \; cm^2 V^{-1} s^{-1}$	μ_h/μ_e
P1 ^a	0.3	DCB, DPE 1 vol%, PHQ <i>m</i> -xylene, DPE 1 vol%	783 745	15.3 15.5	14.9 15.1	59 62	7.0 7.2	$\begin{array}{c} 3.8 \times 10^{-4} \\ 4.2 \times 10^{-4} \end{array}$	$\begin{array}{c} 3.6 \times 10^{-4} \\ 4.3 \times 10^{-4} \end{array}$	1.05 0.97
	16.4	DCB, DPE 1 vol% <i>m</i> -xylene, DPE 1 vol%	2230 2150	4.1 4.1	n/a n/a	38 38	3.4 3.3	n/a n/a	n/a n/a	n/a n/a
P2 ^b	0.3	DCB <i>m</i> -xylene, DPE 0.5 vol%	912 907	13.3 11.9	11.6 10.7	53 52	6.4 5.7	$\begin{array}{c} 2.2 \times 10^{-4} \\ 1.3 \times 10^{-4} \end{array}$	$\begin{array}{c} 1.9 \times 10^{-4} \\ 2.4 \times 10^{-4} \end{array}$	1.16 0.54
	16.4	DCB <i>m</i> -xylene	3269 3624	2.0 2.0	n/a n/a	37 46	2.4 3.3	n/a n/a	n/a n/a	n/a n/a

^a P1: [70]PCBM ratio – 1:2 (by weight), film thickness ca 170 nm, films annealing temperature 95 °C.

^b P2: [70]PCBM ratio – 1:1.5(by weight), film thickness *ca* 120 nm, films annealing temperature 95 °C.

Generally, the blend films based on benzothiadiazole-containing polymer **P1** are more uniform and exhibit smoother surface than the **P2**/[70]PCBM films. The root mean square (RMS) surface roughness values were 1.65 nm and 2.22 nm for **P1**/[70] PCBM films deposited from DCB and *m*-xylene, respectively. On the contrary, **P2**-based films processed from DCB as well as *m*xylene had a rougher surface with RMS of 2.96 nm and 2.85 nm, respectively. Such higher surface roughness is unfavorable for effective exciton dissociation and charge transport to the electrodes. Thus, non-optimal composite morphology seems to be the main reason for the lower J_{SC} and FF values observed for **P2**-based solar cells.

Moving toward the development of the large-area devices, we fabricated modules with the total area of 25 cm² consisting of four series-connected cells. The active area of the modules was 16.4 cm². Active layers were blade-coated in air under the optimized conditions found for small-area OSCs. The photovoltaic parameters of large-area devices are summarized in Table 2, *J*-V curves are shown in Fig. S13 (ESI). The modules based on conjugated polymer **P1** exhibited modest PCE of ~3.3–3.4% for devices

processed from both DCB and xylene. The modules based on polymer **P2** showed higher efficiency when processed from xylene and delivered the PCE of 3.3%. Interestingly, these results were obtained without any buffer layers, which suggests a better interfacial contact between the metal electrode and photoactive layer. These results demonstrate polymers **P1** and **P2** as promising materials for fabrication of large-area OSCs processed from halogen-free solvents under ambient conditions and using R2R-compatible film coating techniques.

Unfortunately, the efficiency of the fabricated modules is still low for practical applications. This issue can be addressed by a rational design of new polymeric materials, e.g. random copolymers comprising benzothiadiazole and benzoxadiazole blocks to reach a good balance between V_{OC} and J_{SC} of the devices. Advantages of using statistical copolymers have been demonstrated in a number of previous reports [29,30,31]. Moreover, the module design can also be improved to reduce losses e.g. due to ITO series resistance. Furthermore, the combination of the developed polymers **P1** and **P2** with low-bandgap non-fullerene acceptors might also improve the performance of solar cells.

Please cite this article as: P. M. Kuznetsov, S. L. Nikitenko, I. E. Kuznetsov et al., Thiazolothiazole-based conjugated polymers for blade-coated organic solar cells processed from an environment-friendly solvent, Tetrahedron Letters, https://doi.org/10.1016/j.tetlet.2020.152037

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Fig. 3. J - V curves (**a**) and EQE spectra (**b**) of solar cells based on **P1** and **P2** under optimal conditions.

Conclusion

In conclusion, we have synthesized and characterized two novel conjugated polymers comprising thiazolothiazole building block combined with thiophene donor and benzothiadiazole (**P1**) or benzoxadiazole (**P2**) acceptor units. Organic solar cells and larger-area photovoltaic modules based on polymers **P1** and **P2** were successfully fabricated from DCB and halogen-free *m*-xylene solvents using scalable blade coating technique. These devices delivered encouraging efficiency of ~7%, thus demonstrating the designed polymers as promising materials for large-area organic photovoltaics processed from environment-friendly solvents.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Russian Science Foundation (project No.18-73-00095). We thank Dr. A Kozlov and Dr. E. Khakina for providing interfacial buffer layer materials.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2020.152037.



Fig. 4. AFM height images for (a) **P1**/[70]PCBM blends processed from DCB with 1% DPE and coated with PHQ buffer and (b) the same films processed from *m*-xylene with 1% DPE; (c) **P2**/[70]PCBM blends processed from DCB and (d) the same films processed from *m*-xylene with 0.5% DPE.

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