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Stability study of quinoxaline and pyrido pyrazine based co-polymers for solar cell applications

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ABSTRACT

We present two co-polymer families; one based on a thiophene-quinoxaline unit and one on a thiophene-pyrido pyrazine unit. Co-polymerization of these monomers with thiophene-hexylthiophene was performed to create polymers with an optical absorption that fully covers the visible part of the solar spectrum with the aim to enhance the solar cell performances of these polymers. We have also studied how increasing the fraction of thiophene-hexylthiophene affects the photo-oxidative stability of these polymers. Thiophene-pyrido pyrazine solar cells displayed increased device efficiency upon addition of the thiophene-hexylthiophene and, in addition, the stability is retained upon inclusion of these units. In contrast, we found that for the thiophene-quinoxaline based co-polymer, both device efficiency and stability decreased with increasing thiophene-hexylthiophene fraction. Moreover, our results indicate that the photo-oxidative stability of the thiophene-quinoxaline co-polymer is independent of the polymer molecular weight as well as of the film thickness.

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1. Introduction

During the last two decades, the interest in polymer solar cells (PSCs) has significantly increased and due to considerable research efforts lab-scale devices now reach power conversion efficiencies of ~9–10% [1,2]. The materials of the active layer of PSCs show high processability due to their solubility in organic solvents and therefore PSCs can be printed with roll-to-roll processes. Hence, they may provide cheaper devices as compared to more traditional silicon-based solar cells, which could compensate for the lower efficiencies of PSCs compared to the silicon-based counterpart. Roll-to-roll processing provides good possibilities for producing large-area, light-weight and flexible devices [3].

It is desirable to improve the absorption of the active layer in order to increase the amount of generated excitons. This can be achieved by several means, for example by making the active layer thicker or by designing the polymer structure to absorb more light, i.e. to make the polymers more black [4]. The latter could be realized by incorporation of an additional moiety in the conjugated backbone of the polymer. Another route that has been employed successfully to increase the absorption is the use of [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) instead of [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) as the acceptor material [5,6].

A big concern associated with PSCs is the lifetime of the devices due to stability issues of the different materials. Long-term stability has to be ensured before commercialization is possible. Degradation can occur in all device layers. Both the aluminum and the ITO electrodes [7–9] as well as the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer [10–12] are susceptible to chemical degradation. Photo-oxidative reactions strongly contribute to the degradation of the active layer, but thermal degradation does also occur [13,14].

Several studies that compare the photo-oxidative stability of various conjugated polymers have been published during the last decade [3,14–16]. The polymer stability depends on several parameters. The distance between the vacuum level and the highest occupied molecular orbital (HOMO) as well as the lowest unoccupied molecular orbital (LUMO) are often mentioned as important factors for the stability [17,18]. Another relevant parameter is the amount of side chains: a reduction in the side-chain content

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improves the overall stability of the polymer [19,20]. For example, one of the most commonly studied polymers, poly(3-hexylthiophene) (P3HT), has a high side-chain content, which gives rise to a relatively poor stability [14,16,20]. Several approaches to improve the stability of PSCs have been proposed such as the use of the inverted device architecture and encapsulation of devices [15,21,22].

In this study, varying amounts of thiophene and hexylthiophene monomers were used in a semi-random co-polymerization process with quinoxaline and pyrido pyrazine monomers, respectively. Here, semi-random co-polymerization refers to that every second unit in the polymer chain is a thiophene without side chains, avoiding twisting of the backbone due to steric interactions. This was done in order to increase the absorption in the gap between the high- and the low-energy absorption peaks of the thiophene-quionoxaline polymer TQ1 and the thiophene-pyrido pyrrazine polymer TQN (Fig. 1); i.e. to make the polymers more black. A random, or in this case a semi-random, co-polymerization would result in a continuous absorbance spectrum in contrast to a spectrum with individual features that would be the result of a block co-polymerization [23]. TQ1 has been shown to be a very promising and easily synthesized polymer with reported solar cell efficiencies up to ~6–7% for conventional devices with $PC_{71}BM$ [24,25]. For inverted devices the reported efficiency is ~5% [26]. It is therefore interesting to evaluate if the inclusion of an extra unit, with complementary absorption, will enhance the performance even further. For TQN:$PC_{71}BM$, the reported device performance is ~1% [27]. Both, TQN and TQ1, display two distinct absorption peaks, one high-energy peak originating from the absorption of aromatic structures and one low-energy peak from the intramolecular charge transfer along the backbone of the polymer. Oligothiophenes absorb at intermediate energies and thus are good candidates for making the two polymers more black. An earlier stability study by Carlé et al. has shown that TQ1 is five times more stable than P3HT, when comparing the decrease in absorbed photons during exposure to 1 sun and 85 °C at ambient atmosphere [20]. Here, we explore to which extent the incorporation of hexylthiophene affects the stability of thiophene-quinoxaline-based co-polymers. In addition, solar cell devices were prepared to investigate how the broadening of the spectra affects the performance.

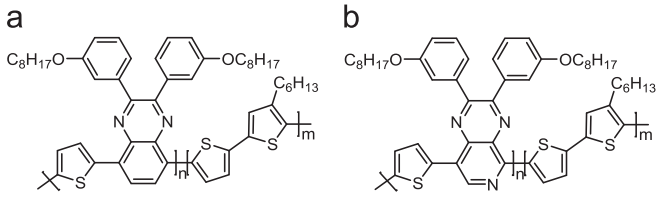

Fig. 1. Molecular structures of (a) TQTHT, $m=0$ corresponds to TQ1 and (b) TQNTHT, $m=0$ corresponds to TQN. In both cases $n=0$ corresponds to THT.

2. Experimental

2.1. Synthesis procedure

2,5-Bis(trimethylstannyl)thiophene and 5,8-dibromo-2,3-bis(3-(octyloxy)phenyl)quinoxaline were purchased from Solarmer Materials Inc. and used as received. Poly[2,3-bis(3-(octyloxy)phenyl)pyrido[3,4–b]pyrazine-*alt*-thiophene] [27], poly[2,3-bis-(3-octyloxy phenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1) [24] and 2,5-dibromo-3-hexyl thiophene [28] were synthesized according to earlier literature. All other reagents and solvents were commercial grade and used as received, purchased from Sigma Aldrich and Acros. Stille coupling was used for all polymerization reactions. All reactions were performed under nitrogen atmosphere. For detailed information on the synthesis, refer to the supporting information, ESI†. The molecular weights of all polymers were measured by gel permeation chromatography (GPC, Table 1). ^1H – NMR spectra were recorded for all polymers using a Varian 400/54/ASP using $CDCl_3$ as solvent (Table 1 and ESI†).

2.2. Thin film preparation

The polymers were dissolved in a solvent mixture of 90 vol% chloroform and 10 vol% chlorobenzene and then spin-coated onto 2×2 cm^2 cleaned glass substrates (thickness ~100 nm unless stated otherwise). The glass substrates were cleaned by sonication in acetone and then isopropanol, followed by rinsing with water, acetone, dichloromethane and finally isopropanol. Prior to the stability measurements, the films were annealed for 15 min at 100 °C and ambient atmosphere but with light protection. The thickness of films was measured with atomic force microscopy in tapping mode using a Digital Instrument Nanoscope IIIa equipped with a type G scanner and a Micro Masch NSC 15 silicon cantilever.

2.3. Stability measurements

Samples were illuminated with 1 sun at ambient atmosphere using an open array solar simulation system from Eye Lighting International (AM 1.5 spectral matching filter, 1000 $W\,m^{-2}$). During illumination, the samples were placed on a heating plate at 85 °C [29] (calibrated with K-type self-adhesive thermocouples from Omega, estimated error ±5 °C; time to reach stable temperature ~30 s). The samples were removed periodically to record the UV–vis absorbance spectra at room temperature with a Perkin Elmer Lambda 900 spectrophotometer.

2.4. Electrochemical spectroscopy

Square-wave voltammetry was carried out at a scan rate of 125 mV s^{-1} using a 0.1 M solution of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile as supporting electrolyte. A CH-Instruments 650 D electrochemical workstation equipped with

Table 1
Molecular weight (M_n), polydispersity index (PDI), HOMO and LUMO levels of the studied polymers as well as THT content of the polymer calculated from NMR data.

Polymer	**M_n** (kg mol^{-1})	**PDI**	**HOMO** (eV)	**LUMO** (eV)	**THT content calculated from NMR** (%)
THT	6	1.6	−5.4	−3.0	100
TQ1	17	2.1	−5.8	−3.4	0
TQTHT ($f_{THT}=30$ mol%)	15	2.3	−5.6	−3.3	32
TQTHT ($f_{THT}=50$ mol%)	17	2.5	−5.5	−3.2	62
TQTHT ($f_{THT}=80$ mol%)	10	2.2	−5.5	−3.3	89
TQN	20	2.4	−6.0	−3.7	0
TQNTHT ($f_{THT}=30$ mol%)	21	2.3	−5.9	−3.6	–
TQNTHT ($f_{THT}=50$ mol%)	16	2.5	−5.6	−3.5	–

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