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New quinoxaline and pyridopyrazine-based polymers for solution-processable photovoltaics

Renee Kroon [a], Robert Gehlhaar [b,*], Timothy T. Steckler [a], Patrik Henriksson [a], Christian Müller [a], Jonas Bergqvist [c], Afshin Hadipour [b], Paul Heremans [b], Mats R. Andersson [a,**]

[a] Chemical and Biological Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden
[b] IMEC vwz, OPV-group, Kapeldreef 75, B-3001 Leuven, Belgium
[c] Biomolecular and Organic Electronics, IFM, Linköping University, SE-581 83 Linköping, Sweden

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ABSTRACT

The recently published quinoxaline/thiophene-based polymer TQ1 has been modified on its acceptor unit, either altering the acceptor strength by incorporating a pyridopyrazine, substitution of the acceptor-hydrogens by fluorine, or substitution of the alkoxy side chain by alkyl. The changes in physical, electronic and device properties are discussed. For the polymers incorporating the stronger acceptors a decreased performance is found, where in both cases the current in the devices is compromised. Incorporation of the pyridopyrazine-based acceptor seems to result in more severe or additional loss mechanisms compared to the polymer that incorporates the fluorine atoms. A similar performing material is obtained when changing the alkoxy side chain in TQ1 to an alkyl, where the solar cell performance is mainly improved on the fill factor. It is demonstrated that the standard TQ1 structure is easily modified in a number of ways, showing the versatility and robustness of the standard TQ1 structure and synthesis.

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1. Introduction

During the last few decades, utilizing polymers as the light harvesting material in bulk heterojunction solar cells has been under intensive research [1–3]. The main driving force for this is that polymers offer the advantage of cost-effective production of large area solar cells via either a roll to roll process or inkjet printing [4,5]. Other advantages about polymer-based solar cells are that the polymer structure can easily be chemically modified and fine-tuned, and the devices can be light-weight and flexible, thereby opening up numerous commercial applications. The prediction is that the power-conversion efficiency of these organic material-based devices needs to achieve 10% efficiency in modules before the concept becomes commercially viable [6]. Currently, the best cells achieve an efficiency of about 8% in the lab [7–9] while research is still ongoing to get more insight in the loss mechanisms that exist in this type of solar cells, and to improve efficiency and lifetime of these polymer-based solar cells.

Recently, a polymer incorporating alternating thiophene-donor and quinoxaline-acceptor units has been reported by our group [10]. This polymer, known as poly[2,3-bis(3-(octyloxy)phenyl)quinoxaline-alt-thiophene] (TQ1) achieved good efficiencies (up to 6%) in solar cells that were based on a TQ1 and [6,6]-Phenyl C_{71} butyric acid methyl ester ([70] PCBM) blend. In this manuscript we present new synthetic possibilities with this type of polymer, and investigate the influence of structural alterations influence physical and electronic properties. Therefore, the structure of TQ1 has been slightly modified, either the acceptor structure directly or on the pendent side chains. This resulted in a series of new polymers (Scheme 1) in which the physical, electronic properties as well as the photovoltaic performance have been evaluated with respect to the structural changes made to TQ1.

The original TQ1 has been modified to the polymer poly[2,3-bis(3-(octyl)phenyl)quinoxaline-alt-thiophene] (TQ-8A) by substituting the octyloxy side chains on the phenyl rings to octyl side chains. This will influence the acceptor strength since a combined resonance and inductive effect is traded for only an inductive effect. However, only a slight influence on the donating power of the benzene substituent on the meta position is expected. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) level of the polymer will therefore only be marginally affected. Since an ether bond is more flexible than a CH_2 and the side-chain length is effectively reduced by one bond length, we expect it to also affect the solubility, molecular weight, packing and blend morphology.

* Corresponding author. Tel. +32 16 28 77 15.
** Corresponding author. Tel.: +46 31 772 3401; fax: +46 31 772 3418.
E-mail addresses: gehlhaar@imec.be (R. Gehlhaar), mats.andersson@chalmers.se (M.R. Andersson).

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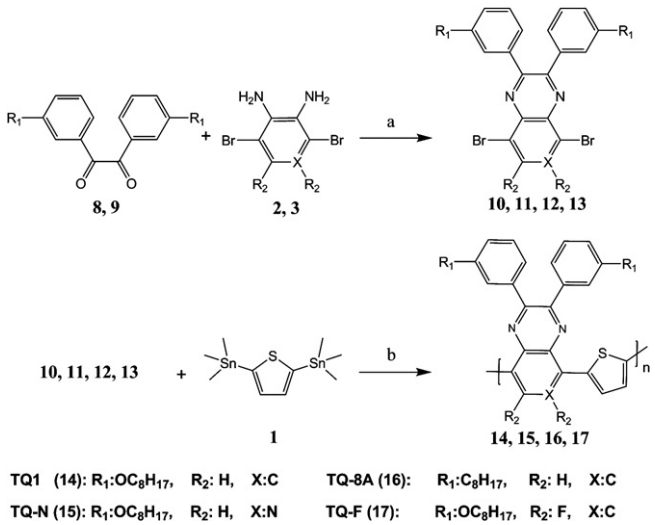

Scheme 1. Chemical structure and synthesis of the polymers. (a) p-TSOH, ethanol, reflux1h, RT18hovernight; (b) Pd2(dba)3, tri-o-tolylphosphine, toluene, 90 1C, 30 min–48 h.

For poly[2,3-bis(3-(octyloxy)phenyl)pyrido[3,4-b]pyrazine-alt-thiophene] (TQ-N) it is expected that the incorporation of an extra electron withdrawing imine-nitrogen will increase the acceptor strength. This will redshift the UV/vis absorption of the polymer because of increased intramolecular charge transfer due to the stronger acceptor [11]. Both the HOMO and the LUMO level will be shifted away from vacuum, increasing the maximum open-circuit voltage (V_{oc}). However, when the electron withdrawing effect is too strong, it results in a charge transfer (CT) state that is too high in energy which promotes different kinds of loss mechanisms [12–14], or decreases the offset between $LUMO_{polymer} - LUMO_{acceptor}$ which in most cases results in decreased current densities [15,16]. Incorporation of the pyridopyrazine will result in a more asymmetric polymer backbone, where the orientation of the nitrogen along the backbone will be the cause of this irregularity. This will influence the thermal properties and possibly the solid state packing.

A final alteration is the incorporation of two fluorine atoms on the acceptor in poly[6,7-difluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline-alt-thiophene] (TQ-F), which is an interesting structural change due to the unique features of the C–F bond. The C–F bond is able to undergo interactions between other atoms (phenyl–perfluorophenyl-(strong), C…H, F…F and C–F…π_F (all weak)) [17,18], possibly decreasing the spacing between polymer chains, inducing some additional ordering and improvement of charge transport. Fluorine itself has a very small radius, slightly larger than a hydrogen atom but the torsion angle will still be slightly affected, which will broaden the energy gap [19]. Also, even though fluorine incorporation usually decreases solubility, it is equally possible that the increased torsion angle induces more flexibility in the backbone, increasing solubility and molecular weight. Using fluorine has a similar effect on the energy of the charge-transfer state due to the electron-withdrawing nature of the fluorine (energy levels away from vacuum), like the pyrido-pyrazine-based acceptor used in TQ-N. However, the net effect of the torsion angle, possible additional ordering and the electron-withdrawing nature is difficult to predict. Some other important features about fluorine are that it is very electronegative, creating a partial ionic bond with carbon that has a high bond dissociation energy which could improve the environmental stability. Also, due to the creation of this partial ionic bond an inversion of the electron cloud distribution is induced [20].

Very recently, several groups explored new polymer materials with a similar incorporation of fluorine, which significantly enhanced the solar cell performance when compared to the solar cell performance of their unfluorinated analogs [7,21–23]. Most notable is that a working device structure has been made by Price et al. which incorporates an extremely thick active layer of 1 μm without severely compromising the fill factor [21].

2. Experimental section

Unless otherwise stated, all reactions were done under nitrogen. Except for 1,4-dibromo-2,3-difluorobenzene (Lianyunggang Acceledev Chem Co. Ltd.) and triflic acid (Fluorochem), all chemicals were bought from Sigma-Aldrich. THF was dried on sodium + benzophenon and distilled prior to use. All other chemicals and solvents were used as received. 3,6-dibromobenzene-1,2-diamine was synthesized according to literature [24]. Experimental procedures can be found in the supporting info. ^{1}H-NMR and ^{13}C NMR spectra have been measured on a Bruker Avance 500 MHz with either $CDCl_3$ or d-DMSO as the solvent. In all cases, the peak values were calibrated relative to tetramethyl silane. *Size exclusion chromatography* (SEC) was performed on Waters Alliance GPCV2000 with a refractive index detector columns: Waters Styvagel HT GE × 1, Waters Styvagel HMW GE × 2. The eluent was 1,2,4-trichlorobenzene. The operating temperature was 135 °C, and the dissolution time was 2 h. The concentration of the samples was 0.5 mg mL^{-1}, which were filtered (filter: 0.45 μm) prior to analysis. The molecular weights were calculated according relative calibration with polystyrene standards. *UV–vis/near IR absorption* spectra were measured with a Perkin Elmer Lambda 900 UV–vis-NIR absorption spectrometer. *Thermo gravimetric analysis* (TGA) measurements were done on a Perkin Elmer TGA7 Thermo Graphic Analyzer, temperature range 30–600 °C, heating rate 10 °C/min. *Differential scanning calorimetry* (DSC) measurements were done on a Perkin elmer Pyris, temperature range 30–300 °C, heating/cooling rate 10 °C min^{-1}, 2nd scan used. *Variable-temperature ellipsometry* was carried out with a RC2 instrument from J.A. Woollam Co., Inc. (USA) at a fixed angle of incidence (70°), equipped with a nitrogen-flushed hot stage. Spin-coated thin films on silicon substrates with a 2.0 nm native silicon oxide top layer were heated by 10 °C min^{-1}. Temperature calibration was performed with an external thin-film temperature sensor (Omega Engineering, UK) that had been glued onto a silicon wafer; error on quoted temperatures is estimated to be ± 3 °C. *Square-wave voltammetry* (SWV) measurements were carried out on a CH-Instruments 650A Electrochemical Workstation. A three-electrode setup was used with platinum wires both as working electrode and counter electrode, and Ag/Ag$^+$ used as reference electrode calibrated with Fc/Fc$^+$. A 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous acetonitrile was used as supporting electrolyte. The polymers were deposited onto the working electrode from chloroform solution. In order to remove oxygen from the electrolyte, the system was bubbled with nitrogen prior to each experiment. The nitrogen inlet was then moved to above the liquid surface and left there during the scans. HOMO and LUMO levels were estimated from peak potentials of the third scan by setting the oxidative peak potential of Fc/Fc$^+$ *vs.* the normal hydrogen electrode (NHE) to 0.630 V [25], and the NHE *vs.* the vacuum level to 4.5 V [26]. *Solar cell fabrication and characterization* Indium–tin-oxide (ITO) coated glass substrates, purchased from Kintec with 10 Ω/sq were cleaned in a sequence of detergent, de-ionized water, acetone and isopropanol, each step for 10 min in an ultra sonic bath. The cleaned substrates were further purified by UV-ozone treatment for 15 min. The substrates were then spin coated with a 0.45 μm filtered poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) solution, Clevios PH500 purchased from HC Starck,

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