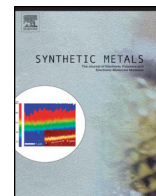




ELSEVIER

Contents lists available at ScienceDirect

Synthetic Metals

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

Mixed side-chain geometries for aggregation control of poly(fluorene-*alt*-bithiophene) and their effects on photophysics and charge transport



Olivia Kettner^a, Andreas Pein^b, Gregor Trimmel^b, Paul Christian^a, Christian Röthel^a, Ingo Salzmann^c, Roland Resel^a, Girish Lakhwani^d, Florian Lombeck^{e,f}, Michael Sommer^e, Bettina Friedel^{a,*}

^a Institute of Solid State Physics, Graz University of Technology, Austria

^b Institute for Chemistry and Technology of Materials, Graz University of Technology, Austria

^c Institute of Physics, Humboldt University, Germany

^d School of Chemistry, Faculty of Science, The University of Sydney, Australia

^e Institut für Makromolekulare Chemie, University of Freiburg, Germany

^f Optoelectronics Group, Cavendish Laboratory, Cambridge, United Kingdom

ARTICLE INFO

Article history:

Received 18 May 2016

Accepted 9 June 2016

Available online 25 June 2016

Keywords:

Polymer

Side-chain engineering

Aggregation

Organic electronics

Charge transport

Photophysics

ABSTRACT

In organic optoelectronics, order of conjugated molecules is required for good charge transport, but strong aggregation behavior may generate grain boundaries and trapping, opposing those benefits. Side chains on a polymer's backbone are major reason for and also tool to modify its morphological characteristics. In this report, we show on the example poly(9,9-dioctylfluorenyl-*co*-bithiophene) (F8T2) that by a combination of two types of side-chains on the backbone of equal number of carbons, one promoting crystallization, another hindering it, organization of the main chains can be controlled, without changing its major properties. We compare the traditional F8T2 derivative with octyl substituent with two modified species, one containing solely 2-ethylhexyl side-chains and another with both types randomly distributed. Thermal characteristics, photophysics and morphology are compared and effects on film formation and charge transport in bulk-heterojunction blends demonstrated on photovoltaic devices utilizing F8T2s as donor and the fullerene derivative ICBA as acceptor material.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Solar cells based on conjugated polymers are a promising class in photovoltaic technology, as they are solution processible, light weight and low cost, compared to commercial silicon solar cells and can be tailored to the required properties via chemical synthesis [1]. The most prominent and efficient active layer configurations are bulk-heterojunction blends, consisting of a polymer as the donor and a fullerene derivative as the acceptor [2a,b,3]. Plenty of effort has been spent in investigating the effects of blend morphology on the performance of devices. In particular, the balance between aggregation and disorder of conjugated polymers in optoelectronic devices remains to be a vital topic [4,5]. Highly ordered regions are beneficial for a small band gap due to

intermolecular coupling and allow efficient charge transport via extended conjugated regions and small hopping distances. However, too large domains limit the dissociation efficiency of excitons in organic solar cells, due to their typically short diffusion length. Further, grain boundaries between ordered regions, especially combined with changing crystallite orientation, as e.g. obtained from aggregate-forming solutions, have detrimental effects on charge transport, because charges have to overcome an energetic barrier to migrate from an ordered aggregate to an amorphous region [6]. It has been shown that this can be unfavorable for charge carriers that may remain and even recombine within the ordered aggregates [4]. Solution to both problems is a careful control of aggregation in the film formation process. Crystallization already within the solution before film deposition should be suppressed [6]. During film formation or via post-deposition treatment, a morphology should be aimed for, which exhibits a network of suitable small ordered regions within

* Corresponding author.

E-mail address: bfriedel@tugraz.at (B. Friedel).

close distance of each other, interconnected by bridging/tying conjugated polymer chain segments [4,5].

Fluorene-based copolymers are highly attractive candidates for OPV, as they offer high charge carrier mobilities and high absorption coefficients in the relevant solar spectrum, accompanied with good processability and high chemical stability [7]. Their properties, in particular the band gap, can be tuned by combination of the electron-deficient fluorene unit with an electron-rich monomer unit, which lead to the term donor-acceptor polymer [8]. Poly(9,9-dioctylfluorenyl-co-bithiophene) (F8T2) is one prominent member of this class of polymers. F8T2 shows thermotropic liquid crystalline behavior, which enables well-ordered films, which showed high hole mobilities in field-effect transistors [9]. For the latter reason it has been considered promising for use in photovoltaic devices. Huang et al. studied F8T2 in solar cells blended with PCBM as acceptor, where it promised well-balanced transport of holes (in F8T2) and electrons (in PCBM) throughout the blend [7]. They discovered strong temperature dependence of the blend morphology. While thermal treatment at a relatively low temperature of 70 °C was suitable for formation of a desired bi-continuous morphology, any higher temperatures supported the polymer's strong tendency to form large crystalline aggregates in the blend, surrounded and thus separated by PCBM. This aforementioned morphology is detrimental for efficient exciton dissociation and charge transport. Accordingly, this limits the viability of F8T2 as is. A suitable tool for influencing a polymer's characteristics are the side-chains. For conjugated polymers, these are usually non-conjugated insulating moieties with the primary function to enable solubility for solution processing [10]. In addition, the type of side-chain can affect the materials' thermal properties, such as glass transition and melting temperatures, and even its energy levels [11,12]. Most important from the morphological side of view, steric effects of side-chains may have influence on the interchain (backbone) stacking distance, the crystal structure, even cause backbone torsion and hinder crystallization entirely, depending on their length, orientation or bulkiness, which in consequence has considerable effects on the photophysics and charge transport in these materials and according devices [5,6,10,12–14]. Further, in blends with other materials e.g. fullerene species or other polymers, the side-chains will influence the miscibility and eventual intercalation, i.e. if a molecule (e.g. fullerene) can penetrate and rest within the polymer lattice [11,15,16].

Here, we present an approach to control the aggregation behavior of F8T2 by varying between straight and branched side-chains on the fluorene units. Therefore three F8T2 derivatives with modified side-chains have been synthesized, as shown in the chemical structure in Fig. 1: The material labelled “P1” represents

the commonly used F8T2 derivative with merely straight octyl side-chains. In the polymer “P2”, the straight octyl chains are replaced by branched 2-ethylhexyl side-chains. Finally, material “P3” has mixed side-chains, i.e. the fluorene units hold either two straight or two branched side-chains in a statistically alternating fashion. The idea behind these structures is illustrated schematically in Fig. 1.

While the straight octyl chains have the ability to interdigitate in a “zipper-like” structure and thus crystallize very strongly (typical for standard F8T2), branched side-chains are more bulky, and thus force a larger backbone distance in the interplanar and the head-to-head (“end-to-end” stacking) direction. The idea behind the third polymer is to *break* the side chain symmetry by the combination of bulky branched groups hindering interdigitation and straight chains forcing the backbones even further apart. Thereby the number of 8 carbon atoms in the side-chain has been kept equal for comparability, as only the side-chain geometry, but not any other variables were meant to be changed. The three materials **P1**, **P2** and **P3** have been characterized in terms of morphological behavior and photophysical properties in their pristine forms and in blends with the fullerene derivative ICBA, which was chosen as acceptor for steric considerations. Due to its larger dimensions (due to the two indene side-groups) compared to C₆₀ or PCBM, it is unlikely to intercalate between the ordered polymer chains. Further, its isomeric nature, i.e. the random orientation of the indene groups, suppresses crystallization of the ICBA. Therefore, any visible effects from the blends have their origin solely in the nature of F8T2 side-chains. Finally, blends of the respective F8T2's with ICBA have been used as active layers in photovoltaic devices and potential effects on charge transport and device physics have been investigated.

2. Experimental details

2.1. Materials

The F8T2 derivatives **P1**, **P2** and **P3** were synthesized by *Suzuki* coupling between 5,5'-dibromo-2,2'-bithiophene and 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester or 9,9-di(2-ethylhexyl)fluorene-2,7-diboronic acid bis(1,3-propanediol) ester, respectively, as demonstrated in *Scheme 1*.

All reactions were carried out under inert atmosphere using Schlenk technique. 1.35 mmol of both monomers were dissolved in 30 mL of anhydrous toluene. Then 50 μL of the phase transfer catalyst, Aliquat 336 were added followed by 6 mL of 2 M aqueous NaOH. After the addition of 15.5 mg tetrakis(triphenylphosphine)-palladium, the reaction mixture was stirred at 90 °C for 48 h. To provide defined end groups the fluorene monomer (37.5 mg, 0.05

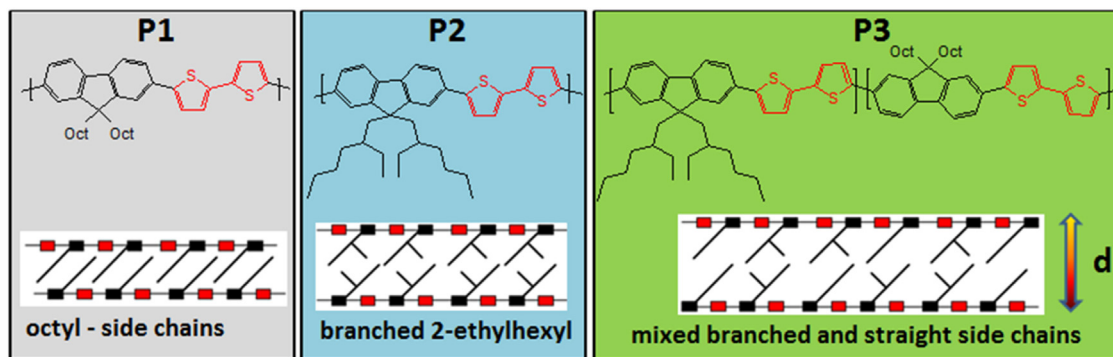


Fig. 1. Chemical structures of the synthesized F8T2 derivatives **P1**, **P2** and **P3** (top), with fluorene unit marked in black and bi-thiophene in red. The schematic drawing (bottom) shows the possible resulting interchain stacking. Fluorene units are represented by black rectangles with one side-chain visible (sterical view) and the bi-thiophene blocks by red rectangles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/1440078>

Download Persian Version:

<https://daneshyari.com/article/1440078>

[Daneshyari.com](https://daneshyari.com)