Reactive & Functional Polymers 86 (2015) 16–26

Contents lists available at ScienceDirect

Reactive & Functional Polymers

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

Towards continuous junction (CJ) organic electronic devices: Fast and clean post-polymerization modification by oxidation using dimethyldioxirane (DMDO)

Florian Glöcklhofer [a], Daniel Lumpi [a,*], Markus Kohlstädt [b,c], Olena Yurchenko [c,d], Uli Würfel [b,c], Johannes Fröhlich [a]

[a] Institute of Applied Synthetic Chemistry (IAS), Vienna University of Technology, Getreidemarkt 9/163, A-1060 Vienna, Austria
[b] Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstrasse 2, D-79110 Freiburg, Germany
[c] Freiburg Materials Research Center (FMF), University of Freiburg, Stefan-Meier-Strasse 21, D-79104 Freiburg, Germany
[d] Institute of Microsystems Engineering (IMTEK), University of Freiburg, Georges Köhler-Allee 103, D-79110 Freiburg, Germany

ARTICLE INFO

Article history:
Received 4 June 2014
Received in revised form 2 September 2014
Accepted 26 October 2014
Available online 11 November 2014

Keywords:
Continuous junction
Post-polymerization modification
Dimethyldioxirane
Functional polymers
Organic electronics

ABSTRACT

An advanced design concept for organic electronic devices relying on functional polymers is presented. The concept aims at realizing a gradual transition from an electron-donating to an electron-accepting material in a specific post-polymerization modification step. Hence, this approach facilitates a straight forward fabrication compared to conventional multi-layer architectures. The synthesis via microwave-assisted Cu(I)-catalyzed azide–alkyne cycloaddition of the reactive polymers based on sulfur, selenium and tellurium as active sites is presented; full characterization of model compounds and polymers is provided. Additionally, a reliable procedure for post-polymerization oxidation applying dimethyldioxirane is developed. Photophysical and electrochemical characteristics of the novel polymers reveal the feasibility but also the challenges of the continuous junction concept.

1. Introduction

Modern organic light-emitting diodes (OLEDs) consist of several layers of materials [1]. While the central emitting layer serves as the primary site of electron–hole recombination, the adjacent hole and electron transporting layers as well as the hole and electron injection layers improve charge carrier transport and eliminate carrier leakage and exciton quenching [2].

In organic photovoltaic devices (OPVs) on the other hand, selective layers improve charge carrier extraction at the electrodes. In addition, prior to extraction two different materials – a donor and an acceptor phase – are required inside the photoactive layer for an efficient separation of the strongly bound electron–hole pairs known as excitons, generated upon illumination [3]. Due to the low dielectric constants in the organic components, exciton dissociation occurs almost exclusively at the donor–acceptor interface [4].

Today, polymer solar cells (PSCs) mainly rely on the bulk heterojunction (BHJ) concept: donor and acceptor material are blended prior to processing and form a bicontinuous interpenetration network within the active layer of the solar cell. This ensures a large surface area between the donor–acceptor interface and, thus, increases the probability for excitons to reach the interface within their limited lifetime [3,5].

However, improving charge separation and transport as well as enhancing the limited control of morphology still remain important issues in OPV development. One goal of current research is to achieve ordered structures within the organic layer of OPVs. Besides decreasing the distance between donor and acceptor material, this aims at solving morphology issues like inclusions, which hinder charge transport to the respective electrodes [6]. The graded donor–acceptor heterojunction concept for small molecules focuses on solving the same issue by a varying donor–acceptor composition across the active layer [7].

In this work, we propose a new approach which potentially enables to overcome the described issues and – in addition – is available by a straight forward procedure. We are aiming at realizing a gradual transition from an electron-donating to an electron-accepting material. The advantages of this novel conceptual

---

* Corresponding author. Tel.: +43 158801163719; fax: +43 15880115499.
E-mail addresses: florian.gloecklhofer@tuwien.ac.at (F. Glöcklhofer), daniel.lumpi@tuwien.ac.at (D. Lumpi), markus.kohlstaedt@ise.fraunhofer.de (M. Kohlstädt), olena.yurchenko@fmf.uni-freiburg.de (O. Yurchenko), uli.wuerfel@ise.fraunhofer.de (U. Würfel), johannes.froehlich@tuwien.ac.at (J. Fröhlich).

http://dx.doi.org/10.1016/j.reactfunctpolym.2014.10.006
1381-5148/

design for organic electronic devices as well as the intended steps of device fabrication are discussed in detail.

In addition, functional electron-donor polymers suitable for post-polymerization modification allowing for such a continuous junction (CJ) concept were developed and are presented.

The CJ concept and, therefore, the developed materials are of relevance for a broad community in the field of organic electronics. In addition to OPV applications, the CJ concept also represents a valuable strategy in OLED fabrication and may significantly simplify the current multi-layer device architecture.

2. Experimental

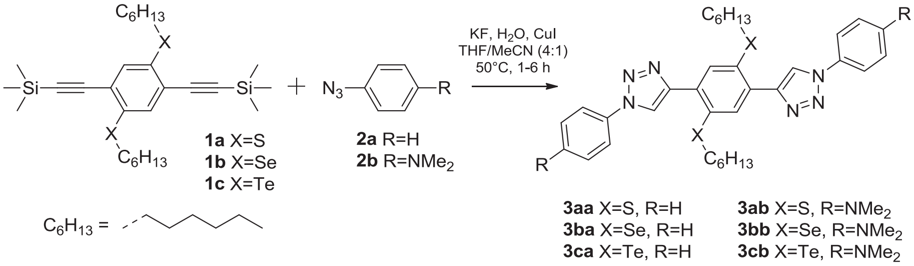
2.1. Materials

Oxidizable substituents – preferably chalcogenide substituents – attached to a conjugated polymer backbone are required for post-polymerization modification using DMDO. However, common materials for OLED and OPV devices do not feature sulfide, selenide or telluride substituents. Therefore, we recently reported on a scalable synthesis of building blocks **1a–c** for such polymers [8]. Azide–alkyne cycloaddition allows for a simple functionalization of such alkynes and therefore was the choice of reaction for the synthesis of model compounds **3aa–cb** and polymers **6aa–cb** bearing oxidizable substituents.

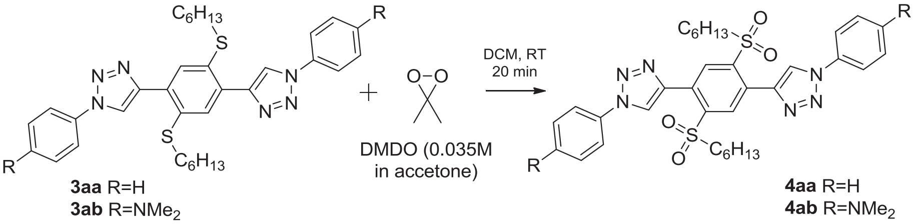
The materials were developed to demonstrate functionalization of the novel building blocks and to demonstrate efficient material modification by applying DMDO. Azidobenzene **2a** and 4-azido-*N*,*N*-dimethylaniline **2b** were used for the synthesis of small molecules (Scheme 1) due to structural similarity to diazides **5a** and **5b**, which were used for polymerization.

Oxidation using DMDO has been investigated for the synthesis of **4aa** and **4ab** (Scheme 2). Dimethyldioxirane (DMDO) is of particular interest for this modification since it enables a stepwise conversion of electronic properties by inversion of electron-donating groups into electron-accepting moieties. This reagent, which can be prepared efficiently on a large laboratory scale [9], fulfills all criteria for a successful realization of a gradual transition from a donor to an acceptor material within a PSC.

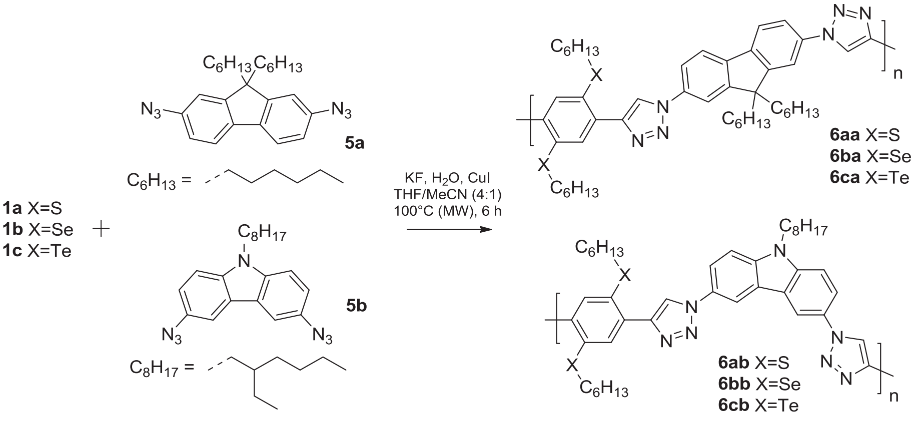
Fluorene and carbazole based diazides **5a** and **5b** were chosen for AA–BB polymerization (Scheme 3). These two structural units are commonly applied in organic electronic materials [10]. Solubility issues are the reason for applying branched side-chains



Scheme 1. Model compounds **3aa–3cb**: Synthesis and molecular structure.



Scheme 2. Model compounds **4aa** and **5ab**: Oxidation using dimethyldioxirane (DMDO).



Scheme 3. Polymers **6aa–cb**: AA–BB polymerization of dialkynes **1a–c** and diazides **5a–b**.