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REVIEW

Ordered conjugated polymer nano- and microstructures: Structure control for improved performance of organic electronics

Lei Zhai[a,b,*], Saiful I. Khondaker[a,c], Jayan Thomas[a,d,e], Chen Shen[a,d], Matthew McInnis[a,b]

[a] NanoScience Technology Center, University of Central Florida, Orlando, FL 32826, USA
[b] Department of Chemistry, University of Central Florida, Orlando, FL 32826, USA
[c] Department of Physics, University of Central Florida, Orlando, FL 32826, USA
[d] Department of Materials Science and Engineering, University of Central Florida, Orlando, FL 32826, USA
[e] CREOL, College of Optics and Photonics, University of Central Florida, Orlando, FL 32826, USA

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Summary Conjugated polymers (CPs), containing conjugated chains with π-electrons delocalized along the polymer backbone, have numerous potential applications in solution processed organic electronics. The charge transport mechanism of CPs and anisotropic charge transport characteristics in organic electronics require the control of CP structures at intra-molecular, inter-molecular and inter-grain level. This review focuses on the technologies that grant the control of the structure and orientation of CP crystal structures, especially the approaches of using graphitic surfaces to guide the crystallization of CPs, and provides an insight into the impact of the orientation of CP nano- and microstructures on CP-based organic electronics such as field-effect-transistors and organic photovoltaics.

Introduction

As we embrace new technologies and appreciate the excitement, convenience and enjoyment of the 21st century, unprecedented challenges including excessive consumption of materials and energy, environmental degradation, and global financial crisis call for all aspects of efforts to improve the global sustainability. Reducing fabrication cost

* Corresponding author at: NanoScience Technology Center, University of Central Florida, Orlando, FL 32826, USA.
Tel.: +1 4078822847.
E-mail address: lzhai@ucf.edu (L. Zhai).

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and improving material performance during operation is one of the major endeavors to surmount these challenges. Solution processed organic devices are of great interest for their potential applicaions in low cost electronics, optoelectronics and clean energy harvest because of their ease of processing, cost effective fabrication, light weight, flexibility, ability to cover large areas as well as the potential of constructing desired devices using rationally designed molecules [1—3]. It is predicted that the organic electronic market will be 44.8 billion US dollars globally in 2018 according to a new market report published by Transparency Market Research [4]. Conjugated polymers (CPs), containing conjugated chains with π-electrons delocalized along the polymer backbone, have numerous potential applications in solution processed organic electronics such as organic field-effect transistors (OFETs) [5—12], molecular electronics [13—15] and bulk heterojunction organic photovoltaics (BHJ-OPVs) [16—31], relying on the unique charge transport properties of CPs.

The active material in CP-based organic electronic devices, polycrystalline CP thin films, are usually produced through a dynamic crystallization of CPs from their solutions. The charge transport in such thin films is through intra-molecular, inter-molecular and inter-grain pathways, where grain refers to ordered CP domains. Intra-molecular transport is the fastest transport of charges along the CP chain due to the delocalized conjugated π-orbitals extending along the whole polymer backbone. However, such efficient charge transport can easily be hindered by the disruption of the delocalized π-orbital along the polymer chain by physical (i.e. chain folding) or chemical defects. It is generally believed that, high-planarity, high-purity and defect free polymer chains obtained through rational molecular design would improve the intrachain charge mobility. Because most devices have geometries much larger than the CP chain-length, charge carrier mobility through a CP crystal is limited by interchain charge transport. This occurs via hopping among neighboring π-orbitals through the π—π stacking of polymer chains. Therefore, the charge mobility depends on the conjugated length and π—π stacking distance [32]. Charge transport across the inter-grain interface is the slowest step since the charges have to overcome an energy barrier to move across amorphous regions. The most recent study suggested that the inter-grain charge transport is the rate determining step for the charge transport in polycrystalline CP films (Fig. 1a) [33]. In this study, the charge transport across aggregates that contain smaller domains with short-range ordering of a few molecular units is demonstrated to be important for efficient charge transport. The key to improve the charge transport is not only increasing the crystallinity of CPs but to improving the tolerance of the disorder at grain bounaries or by eliminating the grain boundary. Over the past three decades, due to an understanding of charge transport mechanisms in CPs, the effort to increase CP charge mobility has focused on the optimization of these three charge transport pathways through the molecular design and morphological improvement. The achievement of such effort is clearly demonstrated by improving the charge carrier mobility of CP based OFETs by more than seven orders of magnitude (Fig. 1b) [6,11,34—72].

While most attention was paid to synthesizing CPs with high charge mobility and optimizing the film morphology, the

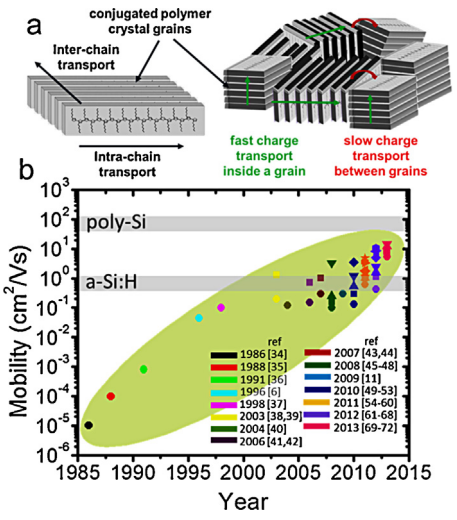

Figure 1 (a) Schematic illustration of charge transport pathways in CP nanowires. (b) The evolution of the field-effect mobility of CP-based OFETs. For comparison, the mobility of amorphous-Si:H and polycrystalline-Si are shown.

orientation of CP crystals and the active material/electrode interfacial properties also have profound effect on the device performance due to the anisotropic charge transport characteristics in organic electronics. For example, it is well accepted that the ideal morphology of the active layer in an OPV device would consist of divided columns of electron and hole transporting materials in close contact with each other. These architectures will allow for efficient charge separation at the donor—acceptor interface and charge transport along each domain to electrodes. The optimization of donor—acceptor interface and morphology has led to significant improvement of device performance [24—31]. Another example is the dependence of charge transport in OFETs on the morphology of the deposited semiconductor layer and the contact between the organic material and electrode interface which determines the charge injection efficiency [73,74]. Therefore, controlling the crystal dimension and orientation is important to improve device performance as well as to design new CPs with high intrechain charge mobility that crystallize with ideal morphologies.

This article overviews the fabrication of ordered CP nano- and microstructures and discusses the impact of structural order on charge transport properties and device performance. Differing from existing review articles regarding CPs [75—79], this review focuses on the technologies that grant the control of the structure and orientation of CP crystal structures, especially the approaches using graphitic surfaces to guide the crystallization of CPs, and provides an insight into the impact of the orientation of CP nano- and microstructures on CP based organic electronics such as field-effect-transistors and organic photovoltaics.

Fabrication of ordered conjugated polymer nano- and microstructures

The effort of building ordered CP nano- and microstructures has been focused on top-down and bottom-up approaches. In top-down approaches, ordered CPs structures are produced