



## Is there a photostable conjugated polymer for efficient solar cells?



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### ARTICLE INFO

#### Article history:

Received 22 October 2014

Received in revised form

5 December 2014

Accepted 20 December 2014

Available online 30 December 2014

#### Keywords:

Low band gap polymers

Photo-oxidation

Degradation mechanisms

Morphology

Organic photovoltaics

### ABSTRACT

The preservation of organic polymer solar cell (PSC) performances over time is of significant concern for their commercial development. A prime PSC degradation pathway is due to inherently photo-unstable conjugated polymers in the photo-active layer which bear continuous illumination in the presence of atmospheric oxygen that diffuses across the encapsulation layers to the whole device. This paper reports on the unexpected photostability of a low band gap polymer, namely poly[(benzo[1,2-*b*:4,5-*b'*]dithiophene)-*alt*-(thieno[3,4-*c*]pyrrole-4,6-dione)] (PBDTTPD), designed for efficient bulk heterojunction PSCs. An approach based on joint computational and spectroscopic studies is implemented to explain the unexpectedly high resistance of PBDTTPD towards photo-oxidation. It is shown that alkoxy side-chains on benzo[1,2-*b*:3,4-*b*]dithiophene (BDT) subunits mitigate the photodegradation of the whole polymer. Furthermore, PBDTTPD favours well-organized structures which inhibit the propagation of the chain oxidation process. Last but not least, results suggest that PBDTTPD is a self-protecting polymer. The first main highlight of this study is that the structure-photostability relationship of conjugated polymers can be dependent on both the macromolecular structure and the morphology of the polymer deposits. The second highlight is that the choice of solubilizing side-chains is a critical factor in the design of stable conjugated polymers for efficient PSCs.

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### 1. Introduction

Polymer solar cells (PSCs) have the potential to become a highly marketable renewable energy technology if the requirements of low cost, high efficiency, and prolonged lifetimes are simultaneously fulfilled. The relative ease of roll-to-roll large-scale production using minute quantities of organic semiconductors facilitates their low cost [1]. With certified power conversion efficiencies near 10% [2], PSCs have now reached the PCE threshold for

commercial applications. The remaining requirement to satisfy, and indeed the most difficult, is that of device stability. PSC modules, continuously exposed to external stress factors such as light, heat, oxygen and humidity, require light-harvesting materials that are stable under severe ageing conditions. The stability of most PSCs reported to date is limited by the instability of the device electrodes, interfaces, and morphology of the active layer [3]. Nevertheless, as significant progress is being made to address these points [4], the stability of future devices will likely be limited by the robustness of the photoactive layer.

The introduction of solubilizing side-chains is mandatory to obtain conjugated polymers that can be processed from solution. However, in terms of photostability, these functionalities are regarded as the Achilles' heel of any polymer. It has been proven that under UV-visible light irradiation, semiconducting polymers start degrading [5–7]. In a

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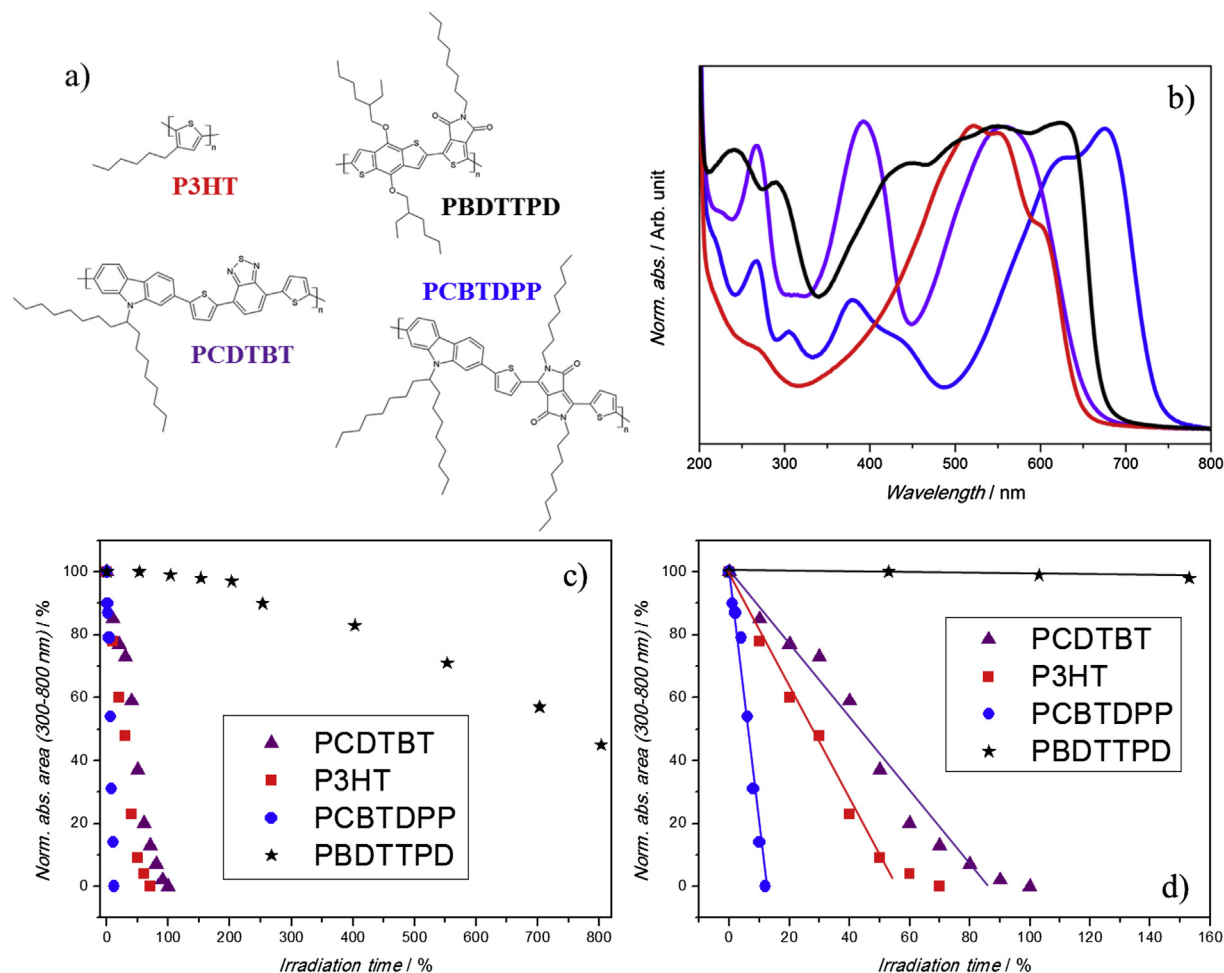
first step, the side-chains are oxidized, initiating a chain radical oxidation reaction that leads to the degradation of the conjugated backbone in later steps. This alters the optical and conducting properties of the photoactive materials and dramatically impacts upon device efficiencies. Given that the photoactive layer drives free-charge carrier generation processes, its stability is of primary importance. In effect, the design of photo-stable conjugated polymers is paramount in overcoming the issue of PSC lifetimes.

The synthesis of a third generation of conjugated polymers with band gaps below 1.6 eV (the so called “low band gap” polymers) has contributed to reach high power conversion efficiencies. These materials are based on alternating electron rich (push) and electron poor (pull) units along the polymer backbone. This push–pull approach increases electron delocalization along the polymer chain and reduces the band gap [8]. A copolymer-based on alternating benzo[1,2-*b*;3,4-*b*]dithiophene (BDT) and thieno[3,4-*c*]pyrrole-4,6-dione (TPD) repeating units, poly[(benzo[1,2-*b*:4,5-*b'*]dithiophene)-*alt*-(thieno[3,4-*c*]pyrrole-4,6-dione)] (PBDTTPD) has elicited particular interest (Fig. 1) [9–12]. A power conversion efficiency of 7.1% and a fill factor of up to 70% were recently obtained for solar cells with active areas of 1 cm<sup>2</sup>. These data are among the highest values reported for such large active area PSC using PC<sub>60</sub>BM as the electron acceptor, a material that is less expensive than PC<sub>70</sub>BM. It is worth noting that upon optimization of the side-chain on the TPD unit, a power conversion efficiency up to 8.5% was recently reported [13]. PBDTTPD was also evidenced as

being thermostable in the dark [11]. These features make PBDTTPD attractive for PSCs and in-depth photochemical studies have to be addressed since highly efficient but poorly photostable materials would be useless.

There are three main concerns with respect the stability of PBDTTPD. First, determine the photostability of PBDTTPD and elucidate the underlying photochemical degradation mechanism. Second, confirm whether or not oxy-alkyl side-chains play an important role in the degradation process. BDT subunits in PBDTTPD macromolecules are flanked by two alkoxy side-chains. A recent paper employed computational studies to select side-chains offering the greatest photostability to the whole conjugated polymer. It was shown that alkoxy side-chains appeared to be better candidates than alkyl side-chains due to the ability of oxygen to destabilize product radicals, and render the degradation process less likely [14]. PBDTTPD appears to be an excellent material to either disprove or confirm the theoretical results. And third, the morphology of a given polymer film, especially with respect to crystalline order, can drastically impact its rate of photodegradation [15]. Therefore the structure–photostability relationship of conjugated polymers can be changed by the morphology of the deposits. PBDTTPD is a good candidate to validate this hypothesis as PBDTTPD has a strong tendency to form aggregates [10].

This study resolves these three points. PBDTTPD films obtained from two different processes were submitted to light irradiation in accelerated artificial photo-ageing devices in ambient air. The



**Fig. 1.** (a) Chemical structures of P3HT (red), the subject of this study PBDTTPD (black), PCDTBT (purple) and PCBTDPP (blue). Initial absorbance (b) and comparison of the photobleaching rate upon photooxidative ageing (c) of PBDTTPD (black), P3HT (red), PCDTBT (purple) and PCBTDPP (blue). (d) Zoom in the first hours of degradation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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