



An efficient and simple tool for assessing singlet oxygen involvement in the photo-oxidation of conjugated materials



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ABSTRACT

Upon exposure to photooxidative conditions, organic materials are susceptible to undergo degradation via processes involving radical oxygen species and/or reaction with singlet oxygen (¹O₂). In this frame, the work herein presents a new and straightforward methodology to clarify the role of highly-reactive ¹O₂ in the photodegradation mechanism of conjugated materials applied in organic electronics. The general methodology consists in the comparison of the infrared signatures of the conjugated materials after the materials are exposed to photooxidative and thermooxidative conditions and *in situ* generated ¹O₂. The methodology was validated by analysing the behaviour of four donor materials commonly used in organic solar cells. Analysis of the degradation mechanism of these materials allowed exemplifying the three possible case scenarios, namely (1) both ¹O₂ and radical oxygen species are involved in the general photooxidation mechanism of the studied material, (2) the material is unreactive towards ¹O₂ and thus this species plays no role in the photooxidation process, and (3) the conjugated material is reactive towards chemically produced ¹O₂ but this species is not the main responsible for the photooxidative degradation of the material. In the latter two cases, a free-radical oxidation process accounts for the photooxidation of the investigated materials. The results derived from this simple, yet enlightening, methodology provide fundamental understanding about the degradation pathways of conjugated materials, which is a key point to develop not only efficient but also stable organic electronic devices.

1. Introduction

To transform the concept of organic solar cells (OSCs) into a competitive technology, the development of highly efficient photoactive materials exhibiting excellent stability is still mandatory. Currently, the efficiency requirement can be considered achieved (at least on a lab scale) by the development of multiple high-performance low band gap materials [1]. However, such organic materials are well known to be highly sensitive to light under ambient conditions, thus making the elucidation of their photo-oxidation mechanisms a key point to develop stable OSCs [2–4].

Upon exposure to photo-oxidative conditions, polymeric materials are generally thought to degrade via a free-radical reaction mechanism [5]. However, singlet oxygen (¹O₂) generation can additionally occur and potentially lead to an alternative degradation pathway. Singlet oxygen generation by molecular triplet state quenching is well admitted in the field of OSCs. Photophysical measurements have revealed that

common electron donor materials can possess a triplet state above the oxygen singlet state (0.98 eV), potentially allowing this kind of energy transfer [6,7]. The use of a molecular fluorescent probe has also directly shown the ¹O₂ photosensitization by donor materials [8,9]. However, the detection of singlet oxygen is not a proof that the so-formed ¹O₂ will react with the material and promote its oxidative degradation.

Here, we present a straightforward procedure to assess the involvement of ¹O₂ in the photo-oxidation mechanism of organic materials. Among the different methods allowing the production of ¹O₂ (microwave, chemical, photo-sensitization... [10]), the dimethylnaphthalene endoperoxide (DMNE) cycloreversion reaction was selected since this method yields ¹O₂ (76%) in solution at room temperature [11]. Under these conditions, the donor material is susceptible to react with the generated singlet oxygen, but not with ground state oxygen. In addition, since the reaction proceeds at room temperature and in the absence of light, the corresponding oxidation products are stable under these conditions and can be readily analysed. Finally,

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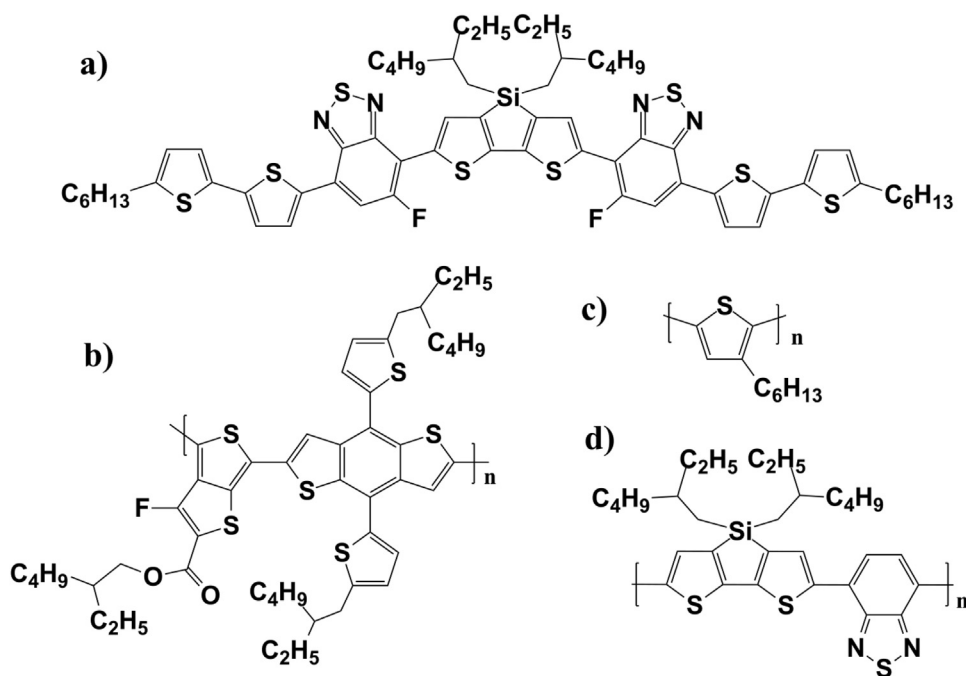


Fig. 1. Chemical structures of the investigated donor materials: a) p-DTS(FBTTh₂)₂, b) PTB7-Th, c) P3HT and d) Si-PCPDTBT.

comparing the infrared signatures of a sample treated with ¹O₂ and samples exposed to photo- and thermo-oxidative conditions allows determining if singlet oxygen attack is an important degradation pathway under photo-oxidation conditions.

In this work, we selected P3HT (poly [3-hexylthiophene]) [8,9,12,13], Si-PCPDTBT (poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-*b*:2',3'-*d*]silole)-2,6-diyl-*alt*-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl]) [6,14] and PTB7-Th (poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl-*alt*-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene)-2-carboxylate-2-6-diyl)]) [7] as model polymers under study due to their distinct behaviours towards ¹O₂ upon photo-oxidation. Indeed, the involvement of ¹O₂ is considered controversial in the case of P3HT photo-oxidation [8,12,15], irrelevant for Si-PCPDTBT photooxidation [16] and, by structural analogy with PTB7, expected to play a major role in the photooxidative degradation of PTB7-Th (Fig. 1) [7]. To assess the scope of our method, we also extended the study to a well-known OSCs small molecule, the so-called p-DTS(FBTTh₂)₂ (7,7'-[4,4-bis(2'-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene-2,6-diyl]bis[6-fluoro-4-[5'-hexyl-(2,2'-bithiophen)-5-yl]benzo[*c*][1,2,5]thiadiazole]) [17,18].

2. Experimental

2.1. Materials

P3HT (M_n = 54–75 kg mol⁻¹, electronic grade 99.9995%), dimethylnaphthalene (DMN) (95%), chlorobenzene (HPLC grade, 99.9%), ortho-dichlorobenzene (HPLC grade, 99%) and chloroform (99.0–99.4%) were purchased from Sigma-Aldrich. Si-PCPDTBT (M_w = 52.8 kg mol⁻¹, PD = 2.85) was provided by BELECTRIC OPV GmbH. p-DTS(FBTTh₂)₂ and PTB7-Th were purchased from 1-Material and methylene blue (≥ 98.5%) was obtained from Fluka. All chemicals were used without further purification.

2.2. Methods

2.2.1. Dimethylnaphthalene endoperoxide (DMNE) preparation

DMNE was prepared according to a procedure reported by Turro et al. [11]. A solution of methylene blue (2 mg) and DMN (1 g) in chloroform (20 mL) was photolysed with a 60 W tungsten lamp under

continuous O₂ bubbling for 3 days at a temperature below 5 °C. Methylene blue was removed by filtration of the solution through Celite. The obtained solution was used without further processing.

2.2.2. Singlet oxygen treatment

The donor materials were dissolved in chloroform at a concentration of 20 g L⁻¹ at ambient temperature and the solutions were then cooled to 5 °C. 50 μL of these solutions was added to 250 μL of the DMNE solution under vigorous stirring and the mixture was allowed to warm to ambient temperature in the dark overnight (around 30 °C was reached on the stirring plate). The solutions were deposited on a KBr substrate and chloroform was allowed to evaporate under vacuum for 24 h. The DMN resulting from the decomposition of the DMNE was washed through acetone dipping for 2 min before infrared analysis of the ¹O₂ treated donor material in the solid state. Furthermore, the infrared analyses confirm DMN washing by disappearance of its vibration bands.

2.2.3. Photo- and thermo-oxidation experiments

Ortho-dichlorobenzene solutions of P3HT and Si-PCPDTBT were prepared. p-DTS(FBTTh₂)₂ and PTB7-Th were dissolved in chlorobenzene. Deposits dedicated to photo- and thermo-oxidative ageing were prepared *via* spin coating on KBr substrates.

Photo-oxidative experiments were performed in a Suntest CPS/XLS Atlas device designed to simulate the AM 1.5 spectrum, especially in the UV domain. UV light below 300 nm and IR light were cut off thanks to the so-called daylight filter from Atlas. The black standard temperature was set at 60 °C which corresponds to a chamber temperature of around 35 °C. Irradiation provided by a xenon lamp from Atlas (NXE1700) was set at 750 W m⁻² in the UV-visible domain.

Thermo-oxidation experiments were carried out in a ventilated oven at 100 °C for the three polymers and at 85 °C in the case of p-DTS(FBTTh₂)₂.

2.2.4. Spectroscopic analysis

UV-visible spectra were obtained on a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere. The absorbance of the samples was measured and integrated in the 300–1000 nm range as indicated in the labels of Figs. S2 to S4 in ESI.

Infrared transmission spectra were recorded with a Thermo

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