

Charge separated states and singlet oxygen generation of mono and bis adducts of C₆₀ and C₇₀



Panagiotis Dallas^{a,*}, Gregory Rogers^{a,1}, Ben Reid^b, Robert A. Taylor^b, Hisanori Shinohara^c, G. Andrew D. Briggs^a, Kyriakos Porfyrakis^{a,*}

^a Department of Materials, University of Oxford, Oxford OX1 3PH, UK

^b Department of Physics, Clarendon Laboratory, University of Oxford, Oxford OX1 3PH, UK

^c Department of Chemistry & Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan

ARTICLE INFO

Article history:

Received 18 August 2015

In final form 7 December 2015

Available online 15 December 2015

Keywords:

Fullerenes

Emission lifetimes

Singlet oxygen

Intersystem crossing

Charge separation

ABSTRACT

We present a series of fullerene derivatives and a study on their photoluminescence properties, complete with their efficiency as singlet oxygen generation photosensitizers. We demonstrate the intramolecular charge transfer between pyrene donor and fullerene acceptor. The opposite effect in decay lifetime measurements is observed for the mono and bis adducts of C₆₀ and C₇₀ for the first time, indicating an interplay between charge-separation and locally excited states. A monoexponential decay was observed for the mono adduct of C₆₀ and the bis adduct of C₇₀, while a biexponential decay was observed for the bis adduct of C₆₀ and the mono adduct of C₇₀. The effect of these molecules as sensitizers of the singlet oxygen radical was tested using detailed 3D excitation photoluminescence maps. A quenching of the singlet oxygen for the C₆₀-mono and C₇₀-bis adducts was observed while a strong photosensitizing effect was observed for the C₆₀-bis and C₇₀-mono adducts.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The surface functionalization of fullerenes is a necessary step for their use in a series of applications in biomedicine as antiviral agents [1], photosensitizers [2], in solar cells as electron acceptor moieties [3] and in quantum computers [4]. The 1,3 dipolar cycloaddition firstly established by the group of Maurizio Prato [5,6] is one of the most widely used reactions for the formation of a series of fulleropyrrolidine derivatives with different anchor groups. These derivatives are easy to design and process, and have recently proved to be remarkably effective as interlayer buffer materials in organic solar cells when placed between the active layer and the cathode [7].

Fullerenes and their derivatives are known to be exceptional electron acceptors that form donor–acceptor complexes [8] and dyads [9] which exhibit photoluminescence emission, albeit with weak intensity, and an intersystem crossing (ISC) to a triplet state. Donor–acceptor dyads have been studied both experimentally and theoretically and include fullerenes linked with porphyrin [9b] or

pyrene rings [10]. Detailed DFT studies on mono adducts of pyrene derivatives indicated a localization of the HOMO levels on the pyrene donor and of the LUMO on the fullerene acceptor [11]. These functional groups change the photophysical properties of the system and result in charge separation states, different intersystem crossing lifetimes and singlet–triplet populations. This is crucial for a number of applications since the charge separated states of donor–acceptor dyads can be used for cell membrane potentials and ion transport control [12a]. The ISC renders fullerenes the most efficient known photosensitizers for the generation of the excited singlet oxygen state ¹O₂ [13].

This combination of properties offers further potential applications as white light emitters [14] and components in quantum information processing devices [15]. However, the fluorescence in fullerenes exhibits low quantum yields because the low lying electronic transitions are only weakly allowed. Surface functionalization of fullerenes has been proven to be an effective way to control the quantum yields of the emission by and the optical patterns through lowering the symmetry of the products.

In our work we present the shift of the emission maximum and change of decay mechanism in mono and bis adducts of the two most widely used fullerenes, C₆₀ and C₇₀, along with their NIR photoluminescence and singlet oxygen generation. A single pathway

* Corresponding authors.

E-mail addresses: panagiotis.dallas@materials.ox.ac.uk (P. Dallas), kyriakos.porfyrakis@materials.ox.ac.uk (K. Porfyrakis).

¹ The first two authors contributed equally to this work.

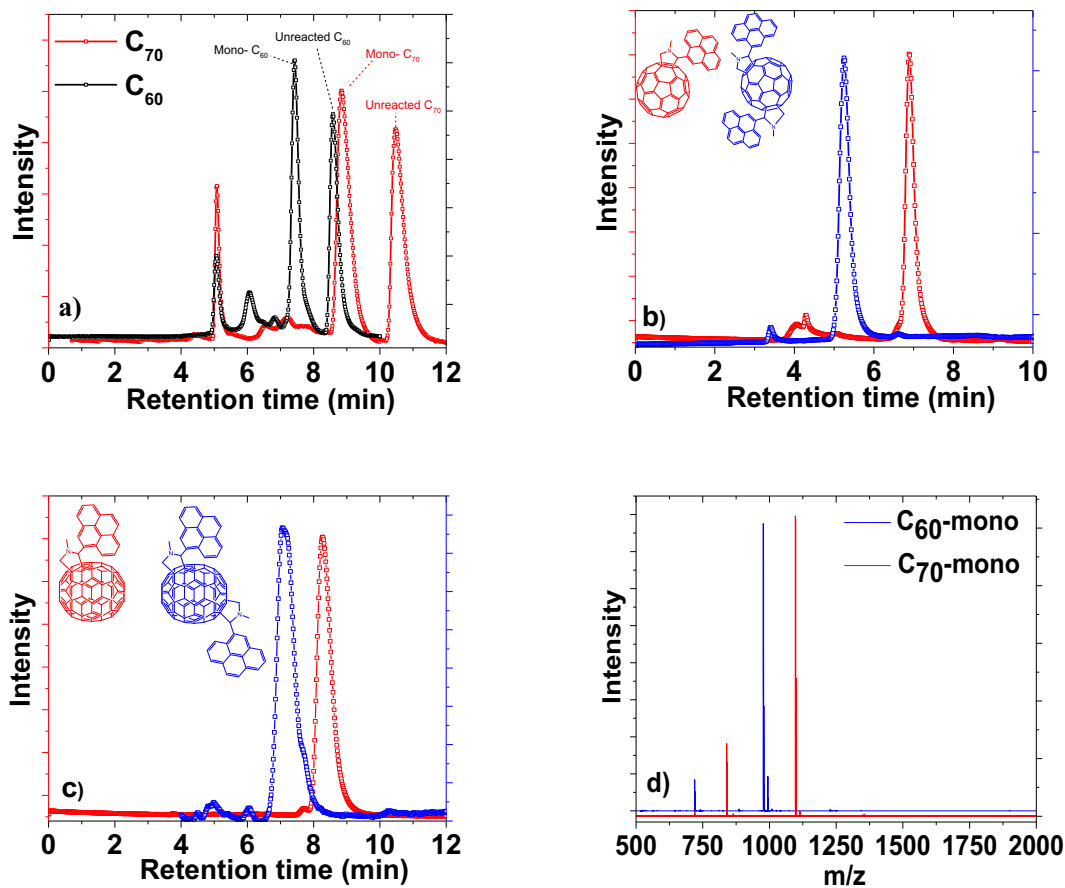


Fig. 1. (a) HPLC chromatographs of the reaction mixture of C_{60} and C_{70} . HPLC of the purified mono and bis adducts of C_{60} (b) and C_{70} (c). (d) Mass spectrometer spectra for the mono adducts of C_{60} and C_{70} . The mass spectra of the bis adducts are given in the supporting information.

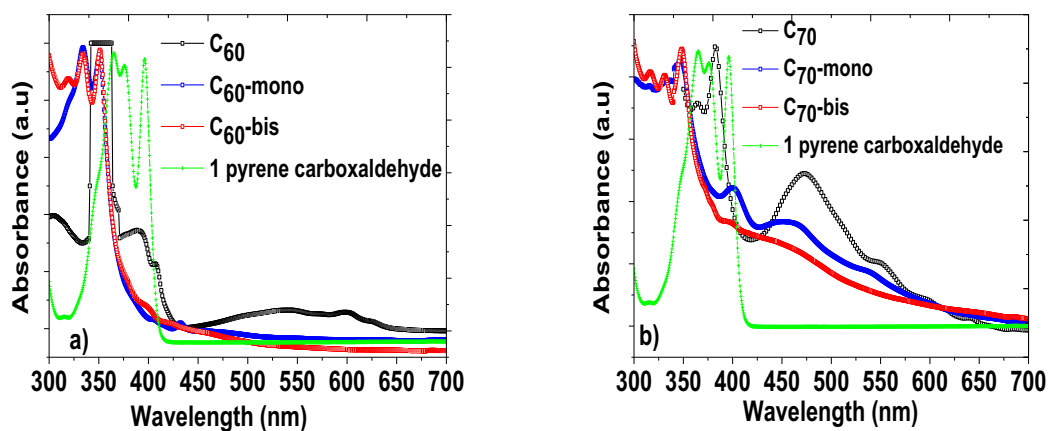


Fig. 2. UV-Visible absorbance spectra of the mono and bis-adducts of (a) C_{60} and (b) C_{70} , in toluene solutions. Green: the 1-pyrene carboxaldehyde precursor. The UV-Visible absorbance spectra of pristine pyrene in both ethanol and toluene exhibiting two peaks at 323 and 336 nm and is presented in Fig. S3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

decay mechanism was observed in the fluorescence decay of the C_{60} mono and C_{70} bis adducts, whilst a two pathways mechanism was observed for the C_{70} mono and the C_{60} bis adducts. This is assigned to the formation of either locally excited or charge-separated states. A similar effect was observed in the intensity of singlet oxygen generation as proven by its 1270 nm emission.

Consequently, the materials can cover a range of emission wavelengths with photosensitizing effects that can be tuned depending on the central cage and the number of functional groups on the surface. Furthermore, the control of charge separated states in a range of organic and inorganic dyads can lead to efficient photocatalysts and light harvesting devices [12b,c].

Download English Version:

<https://daneshyari.com/en/article/5373155>

Download Persian Version:

<https://daneshyari.com/article/5373155>

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