

## Two-photon photosensitization and detection of singlet oxygen within single-ring photonic crystal fibres

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The application of two-photon excitation (TPE) for the photosensitization of singlet oxygen in photodynamic therapy (PDT) increases the penetration depth and spatial selectivity, reducing the photodamage of healthy tissues. The difficulty of detecting photochemical reactions in the extremely small excitation volume of TPE presents a great barrier to the characterization of newly developed photosensitizers tailored for TPE. The direct detection of singlet oxygen ( $^1\text{O}_2$ ) by its intrinsic phosphorescence at 1270 nm is very challenging, because of the extremely low quantum yield of this emission ( $10^{-5}$ - $10^{-7}$ ) and the low quantum efficiency of photodetectors.

Hollow-core photonic crystal fibres (HC-PCFs) are state-of-the-art optofluidic systems that have the ability to solve these problems. The potential of HC-PCF for applications in chemical sensing and photochemistry is beginning to be realised, including the ultra-sensitive detection of fluorescence with attomole sensitivity [1] and sensing luminescence of singlet oxygen at 1270 nm [2]. HC-PCF is particularly promising for the study of two-photon photosensitization since two-photon excitation can be sustained over long path-lengths of within the fibre core [4] without transmission losses.

Single-ring anti-resonant reflection (ARR) fibre is a newly developed type of HC-PCF that significantly reduces the complexity and guidance losses in the core compared to previous generations [4]. We will report an investigation of the use of single-ring anti-resonant HC-PCF for the detection of two-photon photosensitized singlet oxygen, using a well-established fluorescent probe, singlet oxygen sensor green (SOSG) [5]. This novel approach exploits the long path-length over which TPE can be sustained and the co-confinement of both photosensitizer and fluorescent probe along this extended excitation path.

- [1] G. O. S. Williams, T. G. Euser, P. S. J. Russell and A. C. Jones, Spectrofluorimetry with attomole sensitivity in photonic crystal fibres, *Methods Appl. Fluoresc.* 2013, 1, 015003.
- [2] G. O. S. Williams, T. G. Euser, P. S. J. Russell, A. J. MacRobert and A. C. Jones, Highly Sensitive Luminescence Detection of Photosensitized Singlet Oxygen within Photonic Crystal Fibers, *ChemPhotoChem*, 2018, 2, 616-621.
- [3] G. O. S. Williams, T. G. Euser, J. Arlt, P. S. J. Russell and A. C. Jones, Taking Two-Photon Excitation to Exceptional Path-Lengths in Photonic Crystal Fiber, *ACS Photonics*, 2014. 9, 790-793.
- [4] A. M. Cubillas, X. Jiang, T. G. Euser, B. J. Etzold, P. Wasserscheid and P. S. J. Russell, Photochemistry in a soft-glass single-ring hollow-core photonic crystal fibre, *Analyst*, 2017, 142, 925-929.
- [5] X. Ragàs, A. Jiménez-Banzo, D. Sánchez-García, X. Batlloria and S. Nonell, Singlet oxygen photosensitisation by the fluorescent probe Singlet Oxygen Sensor Green, *Chem. Commun.* 2009, 0, 2920-2922.