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Robust triplet–triplet annihilation photon upconversion by efficient oxygen scavenging†

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We hereby present a simple method for reducing the effect of oxygen quenching in Triplet–Triplet Annihilation Upconversion (TTA-UC) systems. A number of commercially available thioethers and one thiol have been tested as singlet oxygen scavengers. Recording of the upconverted emission from a well-studied PdOEP (sensitizer)–DPA (annihilator/emitter) couple has been made over time with steady-state excitation capturing the steady-state kinetics of the TTA-UC process as the solubilized oxygen is depleted by reaction with the scavengers. The efficiency of the TTA-UC process is compared between chemical oxygen scavenging and mechanical removal by inert gas purging or the freeze–pump–thaw method. Selected methods are combined to explore the highest attainable TTA-UC quantum yield. A maximum TTA-UC quantum yield of 21% with the shortest UC onset time was obtained with dimethylthiomethane (DMTM) as the scavenger in an air-saturated solvent and slightly higher quantum yields were obtained in combination with other deoxygenation techniques. Samples containing DMTM displayed little decrease in the quantum yield over four hours of continuous high intensity irradiation, which illustrates the robustness of applying chemical oxygen removal in TTA-UC instead of more time-consuming mechanical processes that usually require specialized equipment.

1. Introduction

Photon upconversion through Triplet–Triplet Annihilation Upconversion (TTA-UC) is a promising technology for the conversion of incoherent low intensity photons to photons with higher frequencies.[1] As illustrated in Fig. 1 the process relies on two molecules: a sensitizer (S) and an annihilator (A). The singlet ground state sensitizer (^{1}S) is excited by low energy photons and forms its first excited triplet state (^{3}S*) through rapid intersystem crossing (ISC). The triplet state energy can be transferred to a ground state annihilator (^{1}A) by the process of Triplet Energy Transfer (TET), thus returning the sensitizer to ^{1}S while the annihilator is excited to its triplet excited state (^{3}A*). Two ^{3}A* can subsequently interact and annihilate so that one annihilator accepts the sum of both excited triplet state energies and populates its singlet excited state (^{1}A*) while the other returns to ^{1}A. The ^{1}A* then radiates the upconverted photon at a wavelength shorter than the photon used to excite ^{1}S, as illustrated in Fig. 1.

The TTA-UC process relies on the diffusion of S and A, vital for the intermolecular TET and TTA processes, which is normally achieved in low viscosity solvents such as toluene.[2] Since
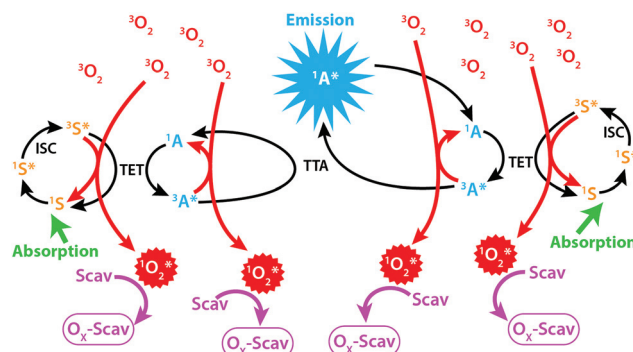

Fig. 1 Illustration of the TTA-UC process in the presence of molecular oxygen and a scavenger (Scav).

the process relies on diffusion one highly desired property of S and A is long lived excited triplet states so that the probability of intermolecular interactions during the lifetime of the excited triplet states is maximized. This property goes, however, hand in hand with a high sensitivity to species capable of quenching the triplet states. One such species is molecular oxygen (O_2)[2] which under atmospheric conditions dissolves in toluene to concentrations that almost completely quench the TTA-UC process (Fig. 1).[3] The field of TTA-UC has evolved at a fast pace over recent years with one of the major goals being the circumvention of oxygen sensitivity while maintaining a high

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upconversion quantum yield.[1,4] This problem is certainly of practical nature but it is still important to be addressed.

Some of the potential solutions to this problem include high-viscosity matrices with low oxygen permeability.[5–8] Similarly, protective coating has been applied to rubbery matrices to isolate the TTA-UC system from oxygen as well as (organic) silica-coating to semi-fluid systems in liposomes.[9,10] So far, the highest robustness has been found in a system without solvent where the annihilator has been modified to act as a viscous solvent itself.[11] This benefits the contact between the interacting species and allows the TTA-UC process to proceed with rates that exceed the diffusion limit, thus lowering the sensitivity of the diffusion limited O_2 quenching. Similar effects have been observed in solid matrices capable of facilitating triplet exciton migration.[12,13] Chemical binding of O_2 during the TTA-UC process has also been demonstrated by the Baluschev group within the chromophores or also with specially made sacrificial scavenging species.[14–16] A similar approach has recently been demonstrated by the Castellano group where polyethylene glycol is used to lower O_2 solubility while oleic acid is used as an antioxidant.[17]

Here we present a convenient way of removing O_2 from a sealed TTA-UC system by simply adding commercially available chemical compounds as scavengers while continuously exciting the TTA-UC system. In the beginning of a typical experiment, the TTA-UC process is quenched by O_2 while simultaneously the O_2 is sensitized to its reactive excited singlet state $(^1O_2^*)$ from where an oxidation of the scavenger is possible.[14,18,19] This is expected to occur through a nucleophile-like mechanism characteristic of oxidation with singlet excited oxygen, unlike the radical reaction mechanism of triplet ground state oxygen which would require a radical initiator.[20–25] The advantage of using commercially available scavengers are several: (i) allowing for usage in larger volumes, (ii) efficient removal of O_2 due to the complete TTA-UC process acting as an O_2-sensitizer and thus also as a scavenging activator, (iii) permanent depletion of O_2 due to an irreversible reaction with the scavenger, (iv) high reproducibility in oxygen removal resulting in higher reproducibility of the TTA-UC efficiency and (v) independence of sample geometry and therefore convenient for applications. The TTA-UC system employed in this study consists of the well known and commercially available palladium(II) octaethylporphyrin (PdOEP) as the sensitizer and 9,10-diphenylanthracene (DPA) as the annihilator.[26–28] This study is evaluated and compared against an already published study by the Castellano group who used the same molecules and concentrations (PdOEP/DPA at 5 μM/ 100 μM) where an UC quantum yield of 16% was reported (defined so that the theoretical maximum Φ_{UC} is 50%).[27]

2. Experimental section

The structures of the sensitizer palladium(II)-octaethylporphyrin (PdOEP) and the annihilator 9,10-diphenylanthracene (DPA) are shown in Fig. 2, while the used scavenger
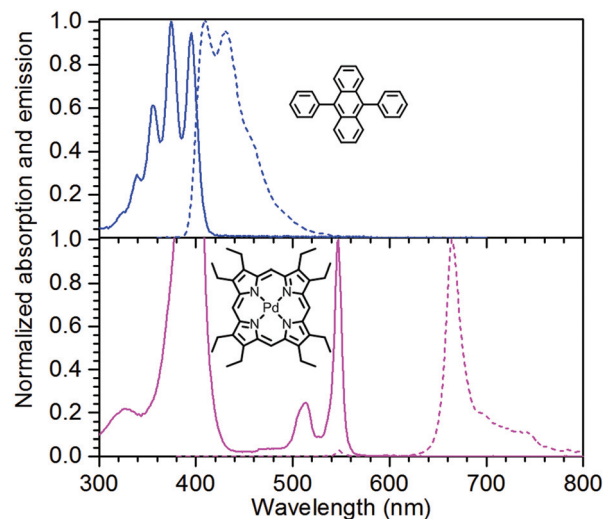

Fig. 2 Absorption (solid) and emission (dashed) spectra of the annihilator DPA (top) and the sensitizer PdOEP (bottom) including molecular structures.

candidates are depicted in Table 1 along with their respective abbreviations. All compounds were used as purchased without any further purification together with PdOEP and DPA in toluene. Two concentrations of the PdOEP/DPA pair are used, 16 μM/500 μM and 5 μM/100 μM, which are referred to as "high" and "low" TTA-UC concentrations, respectively.

Upconversion measurements were performed using a frequency doubled cw Nd:YAG laser (Millenia V, Spectra-Physics) with an output at 532 nm and an average power of 370 mW as the excitation source. The beam diameter was 2.5 mm, determined using burnpaper (ZapIt) and calipers. This gives a photon flux of 2×10^{19} photons per cm^2 per s, which is high enough to ensure that TTA-UC emission is linearly dependent on, and the UC quantum yield (Φ_{UC}) independent of, excitation intensity, provided that O_2 has been thoroughly depleted through scavenging or otherwise.

Emission was captured using a AvaSpec 2048-2 (Avantes) USB fibre spectrometer with a 532 nm notch filter between the sample and the fibre to protect the spectrometer from the intense scattered excitation light. This, in combination with the presence of the sensitizer in the upconversion sample causes perturbation of the upconverted DPA signal through reabsorption, the magnitude of which can change over time if the sensitizer is degraded. In such a case the depletion of the sensitizer has a negative effect on upconversion as the sensitization step becomes less efficient while simultaneously the reabsorption of the UC signal also decreases. In order to avoid these competing perturbing effects, the spectrum of directly excited DPA was scaled to overlap with the non-perturbed region of the UC signal at 460 nm and was used to calculate the upconversion quantum yields.

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Table 1 Structure, name and abbreviation of the used scavengers along with the results of the initial screening process with the onset time and maximum Φ_{UC} results for the low concentration TTA-UC system under the employed excitation conditions

Structure	Full name	Abbreviation	UC onset time (min)	Maximum Φ_{UC}
	2-Mercaptoethanol	BME	44	0.05
	Dimethyl sulfide	DMS	17	0.22
	Dipropyl sulfide	DPropS	16	0.21
	Dimethyl thiomethane	DMTM	2	0.21
	Dimethyl disulfide	DMDS	—	—
	1,2-Dipentyl disulfide	PDFP	—	—
	Cyclohexyl disulfide	ChDS	—	—
	Dibenzyl sulfide	DBS	—	—
	Diphenyl sulfide	DPS	—	—

— No UC emission was detected during 30 min of irradiation.

The Φ_{UC} was determined relative to Cresyl violet perchlorate (Aldrich) dissolved in methanol with a fluorescence quantum yield ($\Phi_f = 0.54$)[29] using eqn (1)

$$\Phi_{UC} = \Phi_R \frac{A_R}{A_x} \frac{F_x}{F_R} \frac{\eta_x^2}{\eta_R^2} \qquad (1)$$

where Φ is the quantum yield, A is the absorbance, F is the integrated emission and η is the refractive index of the solvent. Subscripts R and x denote reference and sample characteristics.

Absorption measurements were performed on a Cary 50 Bio absorption spectrometer and phosphorescence measurements were performed on a Cary Eclipse.

In the initial screening for suitable scavengers, samples were prepared by mixing the prepared TTA-UC solution in toluene with the corresponding scavenger in 2 mL vials with 1 cm internal diameter, a screw cap, a Teflon seal and a parafilm outside, filled so that no air pocket remained. Measurements involving deoxygenation by bubbling of N_2 gas (10 min) were conducted in pyrex test tubes with an internal diameter of 1 cm closed with a rubber septum towards the atmosphere and containing a gas pocket volume in the tube corresponding to twice the sample volume. Measurements involving the freeze–pump–thaw degassing procedure were carried out by repeating the procedure 3 times in a medium vacuum of approximately 1 mbar and melt-sealing the samples with a blowtorch in the same kind of sample tube as for N_2 purged samples. All samples were stirred during measurements in an attempt to maintain any remaining O_2 concentration at equilibrium in the solvent.

For the initial screening of samples that were equilibrated to the atmosphere, the expected initial O_2 concentration was 1.74 mM, estimated using Henry's law constant of $H_{toluene/air} =$ 119 atm M^{-1}. This is under the assumption that the addition of thiols or thioethers does not change the solubility of O_2 to any significant degree in the used solvent mixtures compared to pure toluene. The absorption and emission spectra of the TTA-UC system are shown in Fig. 2.

3.   Results and discussion

Measurements using a TTA-UC system with high concentration ([PdOEP] = 16 μM and [DPA] = 500 μM) in the presence of 500 mM dimethyl sulfide (DMS) as an oxygen scavenger, showed a substantially increased Φ_{UC} to an impressive value of 24% roughly 7 minutes after the start of irradiation at 532 nm, as seen in Fig. 3a. A sample with the same TTA-UC system without a scavenger produced no UC emission for the duration of the irradiation time (30 min). Fig. 4 illustrates the difference in absorbance of the two samples before and after irradiation. The sample without a scavenger suffered severe photodegradation, primarily visible in the region of the DPA absorption (300–400 nm).

A similar value of Φ_{UC} was reached with DMS at a concentration of 10 mM (Fig. 3a). However, the quantum yield dropped more by the end of the measurement which might be due to incomplete oxygen scavenging by the lower concentration of DMS. Degradation was not found to be severe as seen in the absorption spectra before and after irradiation as shown in Fig. S1 in the ESI.†

Using 2-mercaptoethanol (BME), a known oxygen scavenger in the fields of bioscience and microscopy,[30] at 500 mM concentration proved not as efficient in removing oxygen. A maximum Φ_{UC} of about 13% was reached after about 13 minutes (Fig. 3a). The late onset of the UC emission can be attributed to a less efficient scavenger and as a consequence
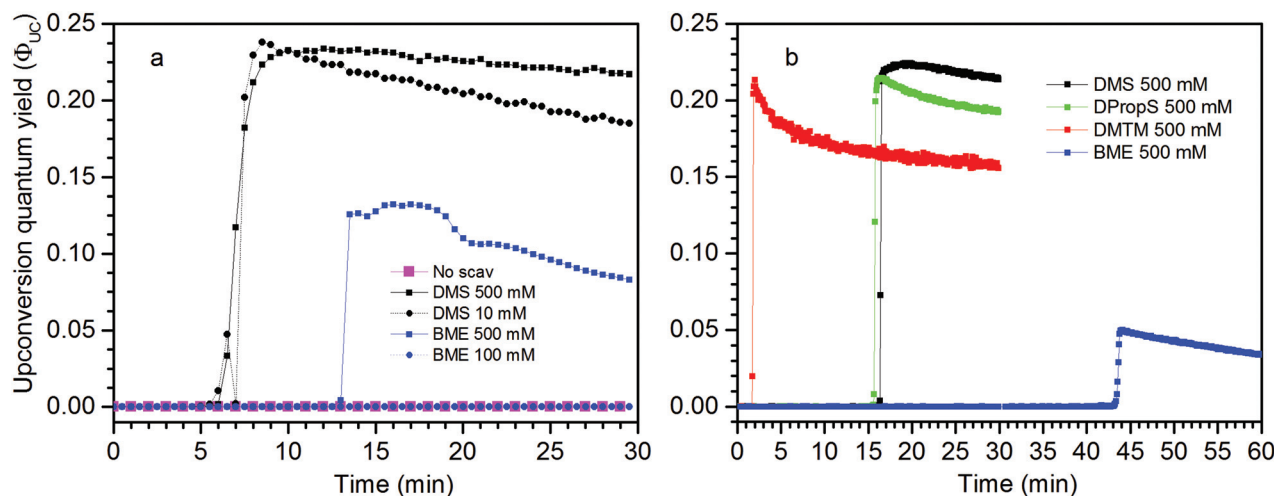
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Fig. 3 The measured Φ_{UC} in filled screw-cap vials during continuous irradiation at 532 nm. (a) High concentration TTA-UC system ([PdOEP] = 16 µM and [DPA] = 500 µM) and (b) lower concentration system ([PdOEP] = 5 µM and [DPA] = 100 µM).
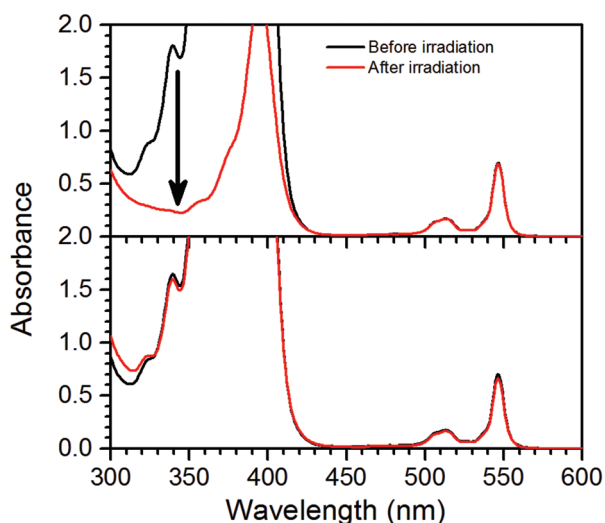

Fig. 4 Absorption spectra before and after the irradiation at 532 nm (30 min) illustrating DPA degradation in the absence of a scavenger (top) and the lack of degradation in the presence of the 500 mM DMS scavenger (bottom).

the sensitizer and annihilator are being degraded. As the sensitizer and annihilator concentrations decrease, the O$_2$ sensitization decreases and the conditions for the TTA-UC process fundamentally change resulting in a delay of the UC emission onset as well as lowering of Φ_{UC}. Using even lower concentrations of BME (100 mM), no UC emission was detected and absorption measurements reveal severe degradation comparable to the sample without a scavenger (Fig. S3†).

The TTA-UC system with lower concentrations ([PdOEP] = 5 µM and [DPA] = 100 µM; Fig. 3b), corresponding to the figure of merit with reference to that yielded Φ_{UC} = 16%,[27] was prepared and the highest Φ_{UC} of 22% was obtained with 500 mM DMS. Indeed the UC emission onset emerges later in time (at

around 17 min) which is the result of fewer sensitizers and annihilators serving as sensitizers for O$_2$ and so the scavenging process is slowed down. The maximum Φ_{UC} is still similar to that of the high concentration TTA-UC system which can be attributed to a similar sensitizer/annihilator ratio which is of high importance as it reflects the efficiency of the sensitizer to annihilator Triplet Energy Transfer (TET) process.

Under these conditions dipropyl sulfide (DPropS) was also tested for the O$_2$ scavenging at 500 mM. The UC emission emerges even sooner with DPropS than with DMS at the same concentrations (Fig. 3). Interestingly though, a slightly higher Φ_{UC} and robustness is obtained using DMS with only minor DPA degradation (Fig. S4†) while sooner and not a high Φ_{UC} with lower robustness was obtained with DPropS. In this respect it might seem surprising that there are practically no signs of DPA degradation at all (Fig. S5†) for DPropS.

Dimethylthiomethane (DMTM) produces a much earlier UC emission onset at about 2–3 minutes after the start of irradiation and the TTA-UC system reaches about the same Φ_{UC} as with the other sulfide scavengers with negligible signs of degradation (Fig. S6†), which makes it the best among those scavenger candidates tested here. The DMTM differs from the previously tested scavengers in that it contains two thioether groups. By stoichiometry, two sulfoxide groups may be created in the oxidation reaction with a single O$_2$ which would constitute complete oxidation and scavenging of molecular oxygen.[19] Even though the effective concentration of the thioether groups is twice the molecular concentration for DMTM, it is probably not the main reason for the very early UC emission onset seen in Fig. 3b considering that different concentrations of DMS produced a similar onset time as shown in Fig. 3a. However, the structural proximity of the two thioether groups in DMTM (Table 1) may be of importance as the initial intermediate species of the O$_2$ being attached to one of the thioether groups directly has another thioether group nearby to complete the scavenger oxidation. This is not true for DMS

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and the other similar species containing only one thioether or thiol functional group. In these cases, the initial intermediate persulfoxide species must be long-lived enough to interact with another scavenger in a second diffusion controlled step before complete scavenging of O_2 is achieved.[31–33] The apparent differences in kinetics during the Φ_{UC} onset shown in Fig. 3 between different scavengers and different concentrations of the same scavenger may be attributed to the dynamic oxidation mechanism of the used scavengers, which is known to depend on the structures, steric effects and concentrations of the sulfides. This scientific topic is well studied but the exact details fall beyond the scope of this investigation.[20,24,34–37]

The disulfide compounds 1,2-dipentyl disulfide (PDFP), dimethyl disulfide (DMDS) and cyclohexyl disulfide (ChDS) as well as diphenyl sulfide (DPS) proved inefficient as scavengers as no UC emission was observed and instead severe degradation of the TTA-UC system was observed (Fig. S7–S10†) after 30 minutes of irradiation which is not entirely surprising as they are generally known to be less-efficient $^1O_2^*$ scavengers.[38] Dibenzyl sulfide (DBS) was also tested and proved inefficient as no UC emission was observed, but without any trace of degradation. Instead, the DPA concentration seemed unchanged and new absorption bands arose in the 300–350 nm region (Fig. S11†), consistent with previous observations.[39] A summary of the screening results (Fig. 3b) of all scavenger candidates using the low concentration TTA-UC system is given in Table 1.

An attempt to quantify the O_2 concentration in the irradiated samples was made by preparing 16 µM PdOEP solution with 500 mM DMS (no DPA) and irradiating for 30 minutes. The PdOEP phosphorescence lifetime was then measured using low intensity excitation pulses to minimize the effects of triplet–triplet annihilation between the sensitizers.[40] The obtained fit (Fig. S15†) revealed a lifetime of 112 µs compared to 770 µs which was obtained using the freeze–pump–thaw method for deoxygenation and where PdOEP is considered unquenched.[40] If the bimolecular oxygen quenching rate (k_q) is assumed to be diffusion controlled ($\sim1 \times 10^{10}$ M^{-1} s^{-1} in toluene[41]), then using Stern–Volmer kinetics in eqn (2)

$$\frac{\tau_0}{\tau} = 1 + \tau_0 k_q [O_2] \qquad (2)$$

where τ_0 and τ are the unquenched and quenched lifetimes of the sensitizer, respectively, the O_2 concentration in the sample could be estimated to be 0.76 µM. This is a significant decrease from the air-saturated estimate of 1.7 mM (see the Experimental section). However, due to the high diffusion rate of O_2, even a low concentration is still enough to significantly quench the long-lived triplet excited state of PdOEP.

The robustness of the UC signal over 240 minutes with and without the 500 mM DMTM scavenger was investigated in a N_2-gas purged sample as this is by far the easiest way of deoxygenating a liquid sample. The data in Fig. 5 clearly demonstrate how sensitive a N_2-deoxygenated sample with a septa is for the penetration of O_2 and how well the 500 mM DMTM
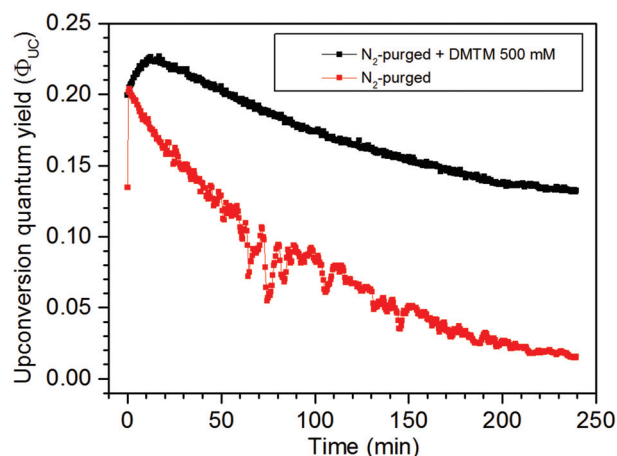

Fig. 5 UC emission of the lower concentration TTA-UC system during long irradiation times for N_2-deoxygenated samples with and without the 500 mM DMTM scavenger.

acts as a scavenger under the same conditions. At first, the sample without a scavenger displays a sharp rise in Φ_{UC} probably as a result of some DPA molecules being served as $^1O_2^*$-scavengers. Apart from this initial rise, both samples start at Φ_{UC} of about 21% but the N_2-purged sample displays a rapid decrease in Φ_{UC} while the sample that also contains the DMTM scavenger displays a gradual rise in Φ_{UC} to about 23% as the residual and entering O_2 is consumed by the scavenger. As the septa does not provide an ideal seal when it comes to O_2, the atmospheric O_2 may eventually enter the sample and the remaining DMTM cannot compensate completely for the leak. The degree of degradation of the TTA-UC system is displayed in Fig. S12 in the ESI.†

The reproducibility of this result was tested at a shorter irradiation time of 30 minutes and repeated four times. A higher time-resolution was also employed to investigate the kinetics features at sub-minute and -second time scales. As seen in Fig. 6a on the minute-scale, in the beginning the N_2-purged samples produce the highest Φ_{UC} and drop over time below the Φ_{UC} of the samples containing the DMTM scavenger. However, at higher time resolutions shown in Fig. 6b, it is evident that the DMTM-containing samples produce a more prompt onset with an initial nick in the UC emission trace which is further resolved as shown in Fig. 6c.

In order to isolate the scavenging effect from the possible O_2 leaks into the sample, the freeze–pump–thaw (FPT) degassing method was performed with the low concentration TTA-UC system with and without the 500 mM DMTM scavenger. As seen in Fig. 7, again the sample without a scavenger displays a higher Φ_{UC} initially and then drops far below that of the DMTM-containing sample. One possible explanation for this observation might be that there is a slight excess of the DPA annihilator in the sample than optimally required to quench the sensitizer and so a minor amount of DPA may be utilized to scavenge part of the residual O_2 in the sealed sample without resulting in a major Φ_{UC} loss. However, the

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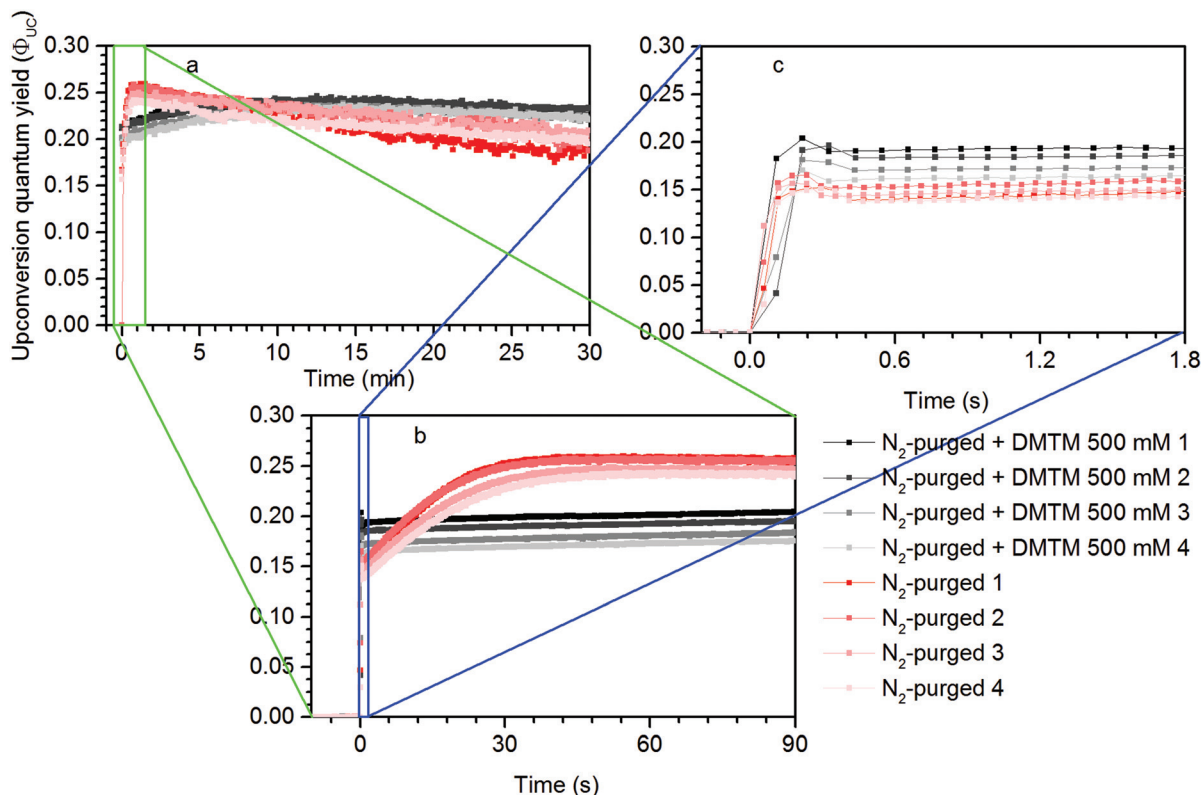
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Fig. 6 UC emission traces of four repeated lower concentration TTA–UC system samples during 30 minutes of irradiation. The experiment compares N$_2$-deoxygenated samples with and without the 500 mM DMTM scavenger during (a) the complete 30 minutes, (b) the first 90 seconds and (c) the first 1.8 seconds of irradiation.
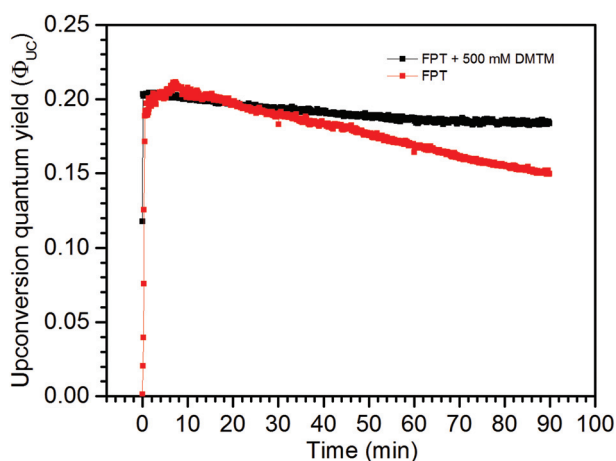

Fig. 7 UC emission of two melt-sealed low concentration TTA–UC system samples after 3 FPT cycles to 1 mbar, with and without the 500 mM DMTM scavenger.

Φ_{UC} of the non-scavenged sample keeps decreasing over time which suggests that there is more O$_2$ in the sample than can be consumed with only excess DPA and so there is a negative effect on the long-time stability of Φ_{UC}. This effect is not nearly as strong with the DMTM-containing sample as the scavenger is being oxidized, and so the scavenged sample attains

an almost constant and robust Φ_{UC} for the duration of the high intensity excitation experiment. The degree of component degradation in this experiment can be found in the absorption spectra shown in Fig. S13 and S14 in the ESI.†

4. Conclusion

Introducing oxygen scavengers as a third species in a TTA-UC system may function well in terms of providing robust upconversion as long as the scavenger is more readily oxidized than the TTA-UC components. Of the series of nine tested scavengers, DMTM seems indeed promising as a singlet oxygen scavenger which may not be so surprising as it most likely is oxidized similar to DMS where the major oxidation product is dimethyl sulfoxide (DMSO).[33,42] We hypothesize that the DMTM lacks a diffusion controlled step in the full reduction of O$_2$ which is probably the reason for its higher efficiency as a scavenger. Also, the end-product's DMSO-like properties are attractive as DMSO is a well known and often used spectroscopic solvent which fulfills one of the demands for the scavenger oxidation product, *i.e.* to not interfere with the TTA-UC system.

We have shown here that it is possible to use thioether- and thiol-like compounds as a third species in a TTA-UC system in order to chemically remove molecular oxygen. However, it is

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crucial for long lasting experiments that the samples are well sealed. More specifically, we have demonstrated by using the commercially available DMTM as the O_2 scavenger that it is possible to achieve and maintain a high Φ_{UC} by applying a few freeze–pump–thaw cycles with a relatively low vacuum followed by a melt-sealing of the sample. This methodology makes it possible to prepare a high-quality and fully fluid TTA-UC sample in less time and without the need for expensive high-vacuum and specialized equipment.

Acknowledgements

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