Electronic Supplementary Material (ESI) for RSC Advances.

# Supporting Information for:

## Modulation of singlet oxygen generation in halogenated BODIPY dyes by substitution at their *meso* position: towards a solvent-independent standard in the Vis region.

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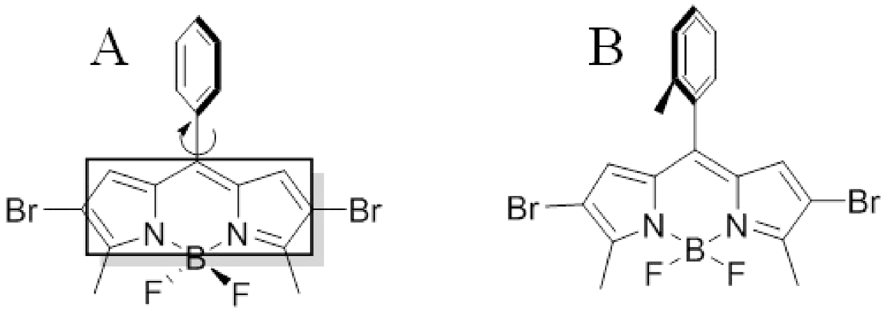

**Figure S1.** Aryl-BDPs rotamers (A) the phenyl group is free rotating and (B) the methyl substitution in ortho position reduces the phenyl free rotation[1–4].

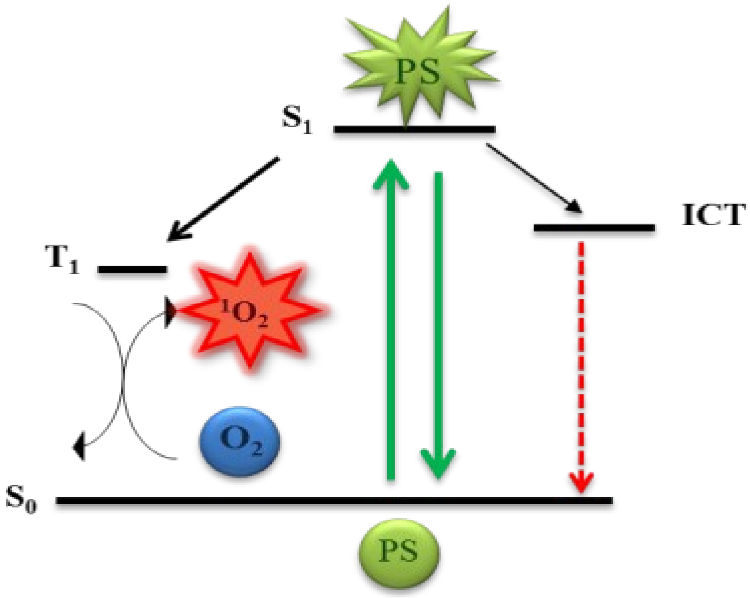

**Figure** S2. Illustrative scheme of the processes involved after the excitation.

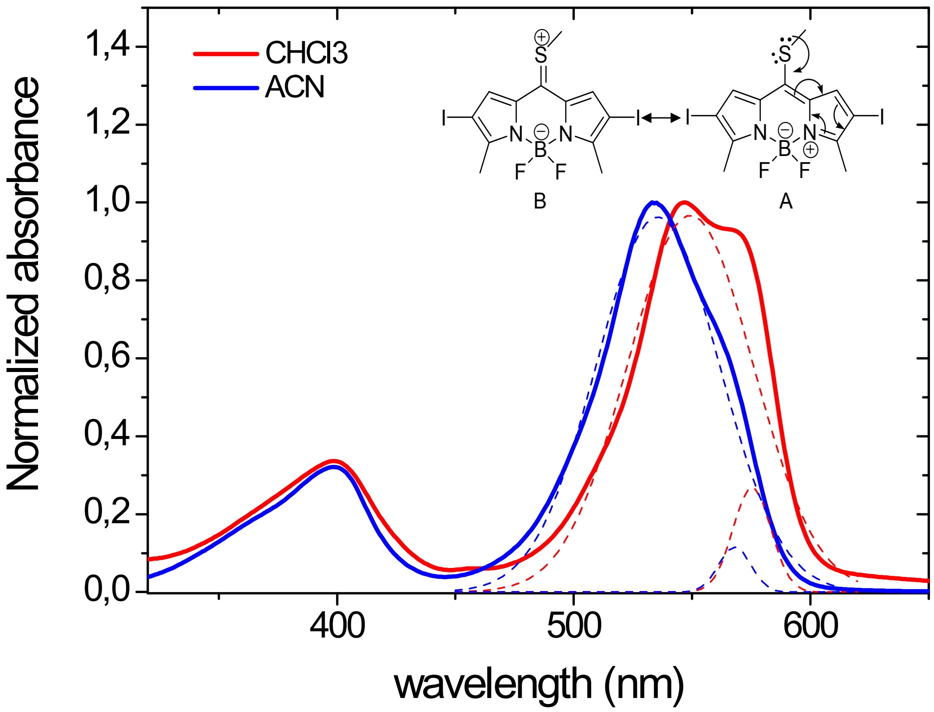

**Figure S3.** Absorption spectra of compound 7 in ACN (blue curve) and chloroform (red curve). The resultant Gaussian curves (dash-curves) after the deconvolution of the main absorption band in both solvents are included. The different resonance structures of the BODIPY core upon electronic coupling with methylthio group at position 8 are also inserted[5]

## Singlet oxygen detection by direct measurement of the luminescence at 1270 nm.

The analysis and quantification of $^1O_2$ by recording its phosphorescence emission signal[6,7] upon continuous monochromatic excitation of the photosensitizer provided the means for determining quantum yields of $^1O_2$ production ($\Phi_\Delta$) and rate constants of $^1O_2$ total quenching by the PS.[8–10] Under continuous irradiation of a PS, the quantum yield of $^1O_2$ emission is given by:

$$\Phi_e = \frac{P_e}{P_a} = \frac{CS_e}{P_0\alpha} \qquad \text{SI 01}$$

where C is a proportionality factor depending on the detection system and on specific parameters of the medium (refractive index, NIR absorbance), $S_e$ is the $^1O_2$ signal intensity, $P_0$ and $P_a$ are the incident photon flux and the photon flux absorbed by the PS ($P_a = P_0\alpha$), $P_e$ is the photon flux emitted by singlet oxygen. $\alpha$ is the absorption factor with A, absorbance of the PS at the wavelength of excitation, given by:

$$\alpha = 1 - 10^{-A} \qquad \text{SI 02}$$

$\Phi_e$ may be also expressed as:

$$\Phi_e = \Phi_\Delta\, k_e\, \tau_\Delta \qquad \text{SI 03}$$

where

$k_e$ ($s^{-1}$) is the rate constant of $^1O_2$ emission (negligible relative to the rate constant of quenching by the solvent in most solvents, $k_d >> k_e$),[11,12] and $\tau_\Delta$ (s) is the singlet oxygen lifetime: in the absence of a quencher, $\sigma_\Delta = 1/ k_d$.

If the $^1O_2$ phosphorescence signals are recorded in the same solvent for the PS investigated and for a standard sensitizer of know $\Phi_\Delta^R$ (and negligible $^1O_2$ quenching: $k_t^Q$ [Q] << $k_d$), the following relation is obtained by combining equations SI 01 and 03 to SI 04 (with Q = PS):

$$\frac{S_e^R P_a^{PS}}{S_e^{PS} P_a^R} = \frac{\Phi_\Delta^R}{\Phi_\Delta^{PS}}\left(1 + \tau_\Delta k_t^{PS}[PS]\right) \qquad \text{SI 04}$$

It should be noted that $\alpha^{PS}$ and $\alpha^R$ (eq. SI 01) should not differ significantly, otherwise the geometry of the system and thus the factor C would be modified and the above relation (SI 04) would not hold.

The plot of $(S_e^R/S_e^{PS})(P_a^{PS}/P_a^R)$ = $f$([PS]) should be linear and values of $k_t^{PS}$ and $\Phi_\Delta^R/\Phi_\Delta^{PS}$ may be obtained from the slope and the intercept of this plot if the value of $\tau_\Delta$ in the solvent used is known.

In the cases where $k_{\mathrm{t}}^{\mathrm{PS}}[\mathrm{PS}] \ll k_{\mathrm{d}}$ (negligible $^1O_2$ quenching by PS in the range of concentrations used), the quantum yield of singlet oxygen production of a PS in a given medium does not depend on the PS concentration (eq. SI 05).

$$\Phi_{\Delta}^{\mathrm{PS}} = \Phi_{\Delta}^{\mathrm{R}} \frac{\mathrm{S}_{\mathrm{e}}^{\mathrm{PS}} P_{\mathrm{a}}^{\mathrm{R}}}{\mathrm{S}_{\mathrm{e}}^{\mathrm{R}} P_{\mathrm{a}}^{\mathrm{PS}}} \qquad \text{SI 05}$$

The apparent values of $\Phi_{\Delta}^{PS}$ ($\Phi_{\Delta app}^{PS}$) at given PS concentrations may be calculated from the ratio of the $^1O_2$ signal intensities (eq. SI 06).

$$\Phi_{\Delta,\mathrm{app}}^{\mathrm{PS}} = \Phi_{\Delta}^{\mathrm{R}} \frac{\mathrm{S}_{\mathrm{e}}^{\mathrm{PS}} P_{\mathrm{a}}^{\mathrm{R}}}{\mathrm{S}_{\mathrm{e}}^{\mathrm{R}} P_{\mathrm{a}}^{\mathrm{PS}}} = \frac{\Phi_{\Delta}^{\mathrm{PS}}}{1 + \tau_{\Delta} k_{\mathrm{t}}^{\mathrm{PS}} [\mathrm{PS}]} \qquad \text{SI 06}$$

In the cases where $k_t^{PS}[PS] \ll k_d$ (negligible $^1O_2$ quenching by the PS in the range of concentrations used), the ratio $S_e^R/S_e^{PS}$ does not depend on the PS concentration and the quantum yield of $^1O_2$ production by the PS is equal to $\Phi_{\Delta app}^{PS}$.

If luminescence intensities are compared from different solvents, the measured intensity $S_e^{PS}$ and $S_e^R$must be corrected for differences in radiative probabilities by multiplying by singlet oxygen phosphorescence lifetimes $\tau_P^{\Delta}$ and for differences in luminescence collection efficiencies, which often depends on $n^2$ (n refractive index) in the reference and the sample solvents (eq. SI 07).[13]

$$Se_{\Delta}^{c} = Se_{\Delta} n^2 \tau_P^{\Delta} \qquad \text{SI 07}$$

where $Se_{\Delta}^{c}$ is the corrected intensity of the luminescence signal by the reference or PS under investigation.

Sometimes a simplified equation is used[14] (Equation SI 08):

$$\emptyset_{\Delta} = \emptyset_{\Delta}(R) \times \frac{\alpha_R}{\alpha_{PS}} \times \frac{Se_{PS}}{Se_R} \times \frac{\tau_{\Delta(R)}}{\tau_{\Delta(PS)}} \qquad \text{SI 08}$$

**Singlet Oxygen probes for indirect determination of $\Phi_{\Delta}$:**

The indirect method to determine the singlet oxygen production consists in the irradiation of a PS solution in the presence of a chemical probe,[15–22] highly selective for singlet oxygen such as 9,10-dimethylanthracene (DMA, Sigma Aldrich). The decrease of the probe signal (absorbance spectra) is recorded with irradiation time.

The sample holder is a spectroscopy quartz cell irradiated directly in the sample compartment of the UV-Vis spectrometer (Perkin Elmer double beam, double monochromator Lambda850) by a 200 W Xe-Hg light source equipped with a monochromator (Apex Monochromator Illuminator with an off-axis F/4 corrected mirror). A Cornerston 260 motorized 1/4m monochromator with a USB communication interface was used to select the irradiation wavelength. Between the light source and the monochromator a CGA-375nm filter and an IR filter were fixed. An LH1 M4 lens was put between the monochromator and the analytical apparatus to collect and concentrate the light beam. The irradiation and the analysis are thus carried out simultaneously (irradiation is perpendicular to the analysis beam). All optical elements were purchased from Newport .

The PS was excited by the proper excitation wavelength from the monochromator (irradiation wavelength chosen to excite the PS near its absorption maxima avoiding any absorption of light by DMA). The kinetics decay of the probe DMA during irradiation was quantified by comparing the spectra (absorbance at 378 nm) during irradiation.

By the indirect method, the rate of disappearance of a probe Q (quencher) when reacted with singlet oxygen is given by SI 09.

$$-\frac{d[Q]}{dt} = k_t[\,^1\mathrm{O}_2][Q] \qquad \text{SI 09}$$

Where the [$^1O_2$] is given by equation SI 10 if it is produced by photosensitization:

$$[\,^1\mathrm{O}_2] = P_a\Phi_\Delta \frac{1}{k_d + k_t^{Ps}[PS] + k_t^{Q}[Q]} \qquad \text{SI 10}$$

$P_a$ (Eisteins $L^{-1}$ $s^{-1}$) is the photon flux absorbed by the PS,[17] and $\Phi_\Delta$ is the singlet oxygen quantum yield. $k_d$ is the rate constant of $^1O_2$ quenching by the solvent, $k_t^{Ps}$ is the rate constant of the total quenching of singlet oxygen by the PS itself and $k_t^{Q}$ is the rate constant of the total quenching of singlet oxygen by the probe (Q). [PS] and [Q] are the respective photosensitizer and probe concentrations. If there is not interference by the reaction products (at the very beginning of the reaction), it is possible to combine Equations SI 09 & 10 to Equation SI 11.

$$-\frac{d[Q]}{dt} = P_a\Phi_\Delta \frac{k_r[Q]}{k_d + k_t^{Ps}[PS] + k_t^{Q}[Q]} \qquad \text{SI 11}$$

This is the equation used for the calculation of singlet oxygen quantum yield of the PS using the indirect method.

$k_t^{Ps}$ is determined by luminescence (direct method), according to the equation SI 06 (using same solvent for the reference and the PS).

If singlet oxygen total quenching by the sensitizer and probe are negligible ($k_t^{Ps}$ [PS] << $k_d$ and $k_t^{Q}$ [Q] << $k_d$) the kinetic analysis is simplified to first order model (Equation SI 12).

$$\ln\,([Q]/[Q]_0) = -P_a\Phi_\Delta\,(k_r/k_d)t \qquad \text{SI 12}$$

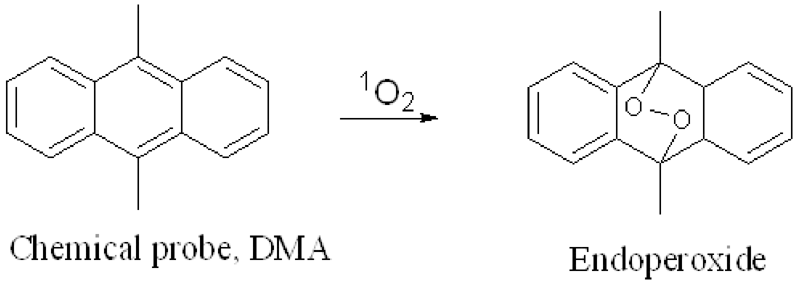

**Figure S4.** The reaction of DMA with singlet oxygen.

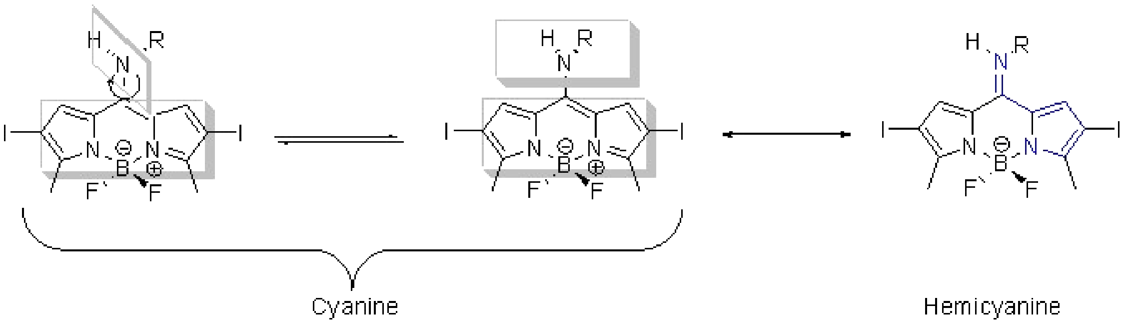

**Figure S5**. BODIPY **8** rotamers[23].

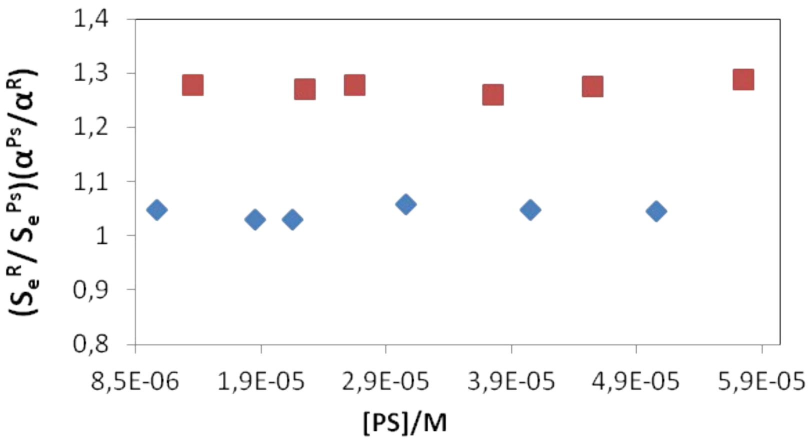

**Figure S6**. Variation of the ratio of the $^1O_2$ emission signal for the reference and PS as a function of the PS concentration in ACN at room temperature: **8** (squares) and **9** (rhombus). Errors: approx 10%.

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