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Supplementary information for:

Methylthio BODIPY as a standard triplet photosensitizer for singlet oxygen production: a photophysical study

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1. General scheme and kinetic equations for singlet oxygen production

Table S1: Kinetic equations of singlet oxygen production and decay (when using O_2, we refer to $O_2(X^3\Sigma_g)$ ground state oxygen)

	Kinetic equation	Process	
Singlet state ($^1PS^*$) formation and decay			
	$\frac{d[^1PS^*]}{dt} = P_a^{PS} - k_{ISC}[^1PS^*] - k_F[^1PS^*] - k_{IC}[^1PS^*]$		Eq. S1
$PS \xrightarrow{h\nu} {}^1PS^*$	P_a^{PS}	Light absorption	Eq. S2
${}^1PS^* \xrightarrow{k_{flu}} PS + h\nu_F$	$-k_{fl}[^1PS^*]$	Fluorescence (radiative decay)	Eq. S3
${}^1PS^* \xrightarrow{k_{isc}} {}^3PS^*$	$-k_{ISC}[^1PS^*]$	Intersystem crossing	Eq. S4
${}^1PS^* \xrightarrow{k_{ic}} PS$	$-k_{IC}[^1PS^*]$	Internal conversion	Eq. S5
$k_{nr}^S = k_{IC} + k_{ISC}$		Non radiative decay	Eq. S6
Triplet state ($^3PS^*$) decay			
	$\frac{d[^3PS^*]}{dt} = -k_r[^3PS^*] - k_{nr}[^3PS^*] - k_{en}[O_2][^3PS^*] - k_{Td}^{O_2}[O_2][^3PS^*] - k_{CT}[O_2][^3PS^*]$		Eq. S7
${}^3PS^* \longrightarrow PS + h\nu_P$	$-k_r^T[^3PS^*]$	Phosphorescence	Eq. S8
${}^3PS^* \longrightarrow PS$	$-k_{nr}^T[^3PS^*]$	Non-radiative decay	Eq. S9
${}^3PS^* + O_2 \longrightarrow PS + {}^1O_2$	$-k_{en}[O_2][^3PS^*]$	Energy transfer	Eq. S10
${}^3PS^* + O_2 \longrightarrow PS + O_2$	$-k_{TD}^{O_2}[O_2][^3PS^*]$	Physical deactivation of ^3PS by O_2	Eq. S11
${}^3PS^* + O_2 \longrightarrow$ others	$-k_{CT}[O_2][^3PS^*]$	Other processes (electron transfer,…)	Eq. S12
$k^T = k_r^T + k_{nr}^T$		Deactivation of the triplet state	Eq. S13
$k_{q,O2}^T = k_{en} + k_{TD}^{O_2} + k_{CT}$		Quenching of the triplet state by O_2	Eq. S14
Deactivation of $^1O_2$ in the absence of a quencher			
	$\frac{d[^1O_2]}{dt} = -k_e[^1O_2] - k_d[^1O_2]$		Eq. S15
${}^1O_2 \longrightarrow O_2 + h\nu_P$	$-k_e[^1O_2]$	Radiative decay	Eq. S16
${}^1O_2 \longrightarrow O_2$	$-k_d[^1O_2]$	Non-radiative decay	Eq. S17
with	$k_e \ll k_d$		Eq. S18
Deactivation of $^1O_2$ in the presence of a quencher Q			
	$\frac{d[^1O_2]}{dt} = -k_e[^1O_2] - k_d[^1O_2] - k_r^Q[^1O_2][Q] - k_q^Q[^1O_2][Q]$		Eq. S19
${}^1O_2 + Q \longrightarrow$ products	$-k_r^Q[^1O_2][Q]$	Chemical quenching of $^1O_2$	Eq. S20
${}^1O_2 + Q \longrightarrow Q + O_2$	$-k_q^Q[^1O_2][Q]$	Physical quenching of $^1O_2$	Eq. S21
$k_t^Q = k_r^Q + k_q^Q$		Total quenching of $^1O_2$ by Q	Eq. S22

The quantum yield of singlet oxygen ($^1O_2$) production ($\emptyset_\Delta$) is defined as:

$$\emptyset_\Delta = \emptyset_T \emptyset_{en} = \emptyset_T \frac{\boldsymbol{k_{en}[O_2]}}{\boldsymbol{k_r^T + k_{nr}^T + k_{q,O2}^T[O_2]}} = \emptyset_T \boldsymbol{P_{O_2}^T f_\Delta^T} \qquad \text{Eq. S23}$$

$$\text{with } \emptyset_T = \frac{k_{ISC}}{k_{fl}+k_{IC}+k_{ISC}} \qquad \text{Eq. S24}$$

and f_Δ^T fraction of PS triplet excited states $^3PS^*$ quenched by O_2 yielding $^1O_2$

$$\boldsymbol{f_\Delta^T = \frac{k_{en}}{k_{q,O2}^T}} \qquad \text{Eq. S25}$$

and $P_{O_2}^T$ fraction of triplet excited states quenched by O_2

$$\boldsymbol{P_{O_2}^T = \frac{k_{q,O2}^T[O_2]}{k_r^T + k_{nr}^T + k_{q,O2}^T[O_2]} = 1 - \frac{\tau_T}{\tau_0^T} = 1 - \frac{I_0^T}{I_T}} \qquad \text{Eq. S26}$$

τ_0^T and I_0^T, τ^T, and I^T the lifetime and emission intensity of the sensitizer triplet excited state in the absence and presence of oxygen respectively.

2. Quantum yields of singlet oxygen production by phosphorescence emission at 1276 nm and quenching of singlet oxygen by MeSBDP

Under continuous irradiation of a sensitizer (PS), the quantum yield of $^1O_2$ emission is given by:

$$\emptyset_e = \frac{\boldsymbol{P_e}}{\boldsymbol{P_a^{PS}}} = \frac{\boldsymbol{CS_e}}{\boldsymbol{P_a^{PS}}} = \Phi_\Delta^{\mathrm{PS}} k_e \tau_\Delta \qquad \text{Eq. S27}$$

with P_e, the photon flux emitted by singlet oxygen (phosphorescence), P_a^{PS} (einstein L^{-1} s^{-1}) the photon flux absorbed by the sensitizer at the wavelength of excitation:

$$P_a^{PS} = P_0(1 - 10^{-A_{PS}}) = P_0 \alpha_{PS} \qquad \text{Eq. S28}$$

P_0, incident photon flux (einstein L^{-1} s^{-1})

C, proportionality factor depending on geometric and electronic characteristics of the detection system and on specific parameters of the medium (refractive index, NIR absorbance),

S_e, the $^1O_2$ signal intensity,

k_e (s^{-1}), the rate constant of $^1O_2$ emission (Eq. S16) and τ_Δ (s) the $^1O_2$ lifetime in the system considered. In the absence of a quencher:

$$\tau_\Delta = {}^1\!/_{k_d} \qquad \text{Eq. S29}$$

with k_d rate constant of $^1O_2$ deactivation by the solvent (Eq. S17, since $k_e << k_d$ in most solvents).[1–3]

In the presence of a quencher that may be the photosensitizer itself (Q = PS),

$$\tau_{\Delta}^{\mathrm{Q}} = \frac{1}{(k_d + k_t^{\mathrm{Q}}[\mathrm{Q}])} \qquad \text{Eq. S30}$$

where k_t^Q (M^{-1} s^{-1}) is the rate constant of $^1O_2$ total quenching (Eq. S 22, sum of physical and chemical quenching) by Q.

Considering a possible quenching of $^1O_2$ by the PS itself (Q = PS), k_t^{PS} and Φ_{Δ}^{PS} may be determined by relative measurements, using a reference sensitizer ($\mathrm{PS_{Ref}}$) of known quantum yield of singlet oxygen production ($\emptyset_{\Delta}^{\boldsymbol{PS_{Ref}}}$). Combining Eqs. S27 to S30, the ratio of the $^1O_2$ luminescence quantum yields for PS and $\mathrm{PS_{Ref}}$ in the same solvent is given by:

$$\frac{\emptyset_{\boldsymbol{e}}^{\boldsymbol{PS}}}{\emptyset_{\boldsymbol{e}}^{\boldsymbol{PS_{Ref}}}} = \frac{\boldsymbol{S_{e,PS}}}{\boldsymbol{S_{e,PS_{Ref}}}} \times \frac{\boldsymbol{\alpha_{PS_{Ref}}}}{\boldsymbol{\alpha_{PS}}} = \frac{\emptyset_{\Delta}^{\boldsymbol{PS}}}{\emptyset_{\Delta}^{\boldsymbol{PS_{Ref}}}} \times \frac{(\boldsymbol{k_d} + +\boldsymbol{k_t^{PS_{Ref}}}[\boldsymbol{PS_{Ref}}])}{(\boldsymbol{k_d} + \boldsymbol{k_t^{PS}}[\boldsymbol{PS}])} \qquad \text{Eq. S31}$$

This expression assumes that the apparatus factors (C) are identical in both cases and that the PS under analysis and the reference are excited at the same wavelength ($P_0^{\mathrm{PS}_{Ref}}/P_0^{\mathrm{PS}}$ = 1). This expression simplifies to Eq. S32 for the phenalenone reference since $k_t^{PS_{Ref}}[PS_{Ref}] \ll k_d$ in the range of concentration considered ($k_t^{Phe} = 3.2\ 10^4\ M^{-1}s^{-1}$).[4]

$$\frac{\boldsymbol{S_{e,PS}}}{\boldsymbol{S_{e,PS_{Ref}}}} \times \frac{\boldsymbol{\alpha_{PS_{Ref}}}}{\boldsymbol{\alpha_{PS}}} = \frac{\emptyset_{\Delta}^{\boldsymbol{PS}}}{\emptyset_{\Delta}^{\boldsymbol{PS_{Ref}}}} \times \frac{\boldsymbol{1}}{(\boldsymbol{1} + \boldsymbol{\tau_{\Delta} k_t^{PS}}[\boldsymbol{PS}])} \qquad \text{Eq. S32}$$

Under these conditions, the plot of ($\boldsymbol{S_{e,PS_{Ref}}}/\boldsymbol{S_{e,PS}}$)($\alpha_{PS}/\alpha_{PS_{Ref}}$) = *f*([PS]) should be linear and give the values of k_t^{PS}. From our results (Figure S7), it may be concluded that $k_t^{PS}[PS] < 0.1 \times k_d$, which led to the upper limit of k_t^{PS} in Table 1.

From Eq. 30, an apparent value of $\emptyset_{\Delta}^{\boldsymbol{PS}}$ ($\emptyset_{\Delta \boldsymbol{app}}^{\boldsymbol{PS}}$) at the given PS concentration may be calculated:

$$\emptyset_{\Delta \boldsymbol{app}}^{\boldsymbol{PS}} = \emptyset_{\Delta}^{\boldsymbol{PS}} \frac{\boldsymbol{k_d}}{(\boldsymbol{k_d} + \boldsymbol{k_t^{PS}}[\boldsymbol{PS}])} = \emptyset_{\Delta}^{\boldsymbol{PS}} \times \frac{\boldsymbol{1}}{(\boldsymbol{1} + \boldsymbol{\tau_{\Delta} k_t^{PS}}[\boldsymbol{PS}])} \qquad \text{Eq. S33}$$

From Eq. 31, when $k_t^{\mathrm{PS}}[\mathrm{PS}] \ll k_d$ (negligible $^1O_2$ quenching by the PS in the range of concentrations used), the ratio $S_{e,PS_{Ref}}/S_{e,PS}$ does not depend on the PS concentration and the quantum yield of $^1O_2$ production by the PS, Φ_{Δ}^{PS}, is equal to $\emptyset_{\Delta app}^{PS}$:

$$\emptyset_{\Delta}^{\boldsymbol{PS}} = \emptyset_{\Delta}^{\boldsymbol{PS_{Ref}}} \frac{\boldsymbol{S_{e,PS}}}{\boldsymbol{S_{e,PS_{Ref}}}} \times \frac{\boldsymbol{\alpha_{PS_{Ref}}}}{\boldsymbol{\alpha_{PS}}} \qquad \text{Eq. S34}$$

3. Determination of the rate constant of quenching of triplet state of MeSBDP by β-carotene as triplet acceptor.

The triplet state of MeSBDP can be quenched by collisions in solution not only by molecular oxygen but also by other triplet acceptors. The triplet acceptor β-carotene was chosen here, since it does not absorb at the excitation wavelength λ_{exc} = 570 nm (Figure S5A) and the energy of its low lying triple state is lower than the triplet state of MeSeBDP. The quenching was studied by time-resolved nanosecond transient absorption experiments at different β-carotene concentrations. In the presence of the triplet acceptor, the triplet lifetime of the MeSBDP decreases (Table S4, Figure S5B). The bimolecular quenching rate constant ($k_{q,car}^{T}$) in chloroform is obtained from the Stern-Volmer plots ${}^{1}/_{\tau_T}$ against β-carotene concentrations (Figure 7B), according to the Stern-Volmer equation:

$$\frac{1}{\tau^T} - \frac{1}{\tau_0^T} = k_{q,car}^{T}[carotene] \qquad \text{Eq. S35}$$

The observed $k_{q,car}^{T}$ was obtained by fitting the decay curve at 425 nm. The rate constants of quenching of triplet state of MeSBDP by triplet acceptors are usually in the time range of the diffusion rates, k_{diff} in a given solvent, determined by Eq. S36

$$k_{diff} = \frac{8\,k_B T}{3\eta} \qquad \text{Eq. S36}$$

where k_B is the Boltzmann constant (1.38×10^{-23} J K^{-1}),

η is the viscosity of the solvent (0.53×10^{-3} Pa·s)

From Eq. S38, k_{diff} in chloroform is 12×10^{9} $M^{-1}s^{-1}$.

The same method was applied for triplet state quenching by O_2.

For the calculation of the singlet oxygen quantum yields ($\emptyset_{\Delta}^{PS}$) of MeSBDP according to Eq. S34 in the experimental section, the values in Table S2 for $\emptyset_{\Delta}^{Ref}$ (PS_{Ref}=PHE) were used as reference.

*Table S2: 1H-phenalen-1-one (PHE) singlet oxygen quantum yield (Φ_{Δ}^{Phe}) from literature (except otherwise stated), singlet oxygen lifetimes (**τ_{Δ}**), rate constant of singlet oxygen quenching by the solvent ($k_d = {}^{1}/_{\tau_{\Delta}}$).*

Solvent	Φ_{Δ}^{Phe}	**τ_{Δ}*** (μs)**	**k_d (s^{-1})**
Cyclohexane	0.92[4]	27 (21±4)	3.70×10^{4}
Toluene	0.92[5]	27 (27±2)	3.70×10^{4}
Dioxane	0.99[6]	30	3.33×10^{4}
Chloroforme	0.98[4]	201 (235±30)	4.98×10^{3}
Dichlorometane	0.96[5]	97 (101±39)	1.03×10^{4}
Acetone	1*	58 (50.5±4)	1.72×10^{4}
Acetonitrile	1[5]	81 (66.7±13.5)	1.23×10^{4}
EtOH	0.92[5]	18 (15.5±3.5)	5.56×10^{4}
MeOD	0.98**	37	2.70×10^{4}
MeOH	0.98 [4]	10 (9.9±0.5)	9.09×10^{4}
D_2O:MeOD (1:1)	1*	45	2.22×10^{4}
D_2O	0.97[5]	n.d.	n.d.

*we have used 1 for acetone and D_2O:MeOD (1:1) as there is not value in the literature
**we have used the same values as MeOH as there is not value in the literature
***Values measured in our group

Table S3: Maximum concentration of PS, $[PS]_{max}$, singlet oxygen lifetime in the considered solvent (τ_{Δ}), constant of singlet oxygen quenching by the solvent (k_d), and maximum rate constant of singlet oxygen total quenching by PS.

Solvent	**$[PS]_{max}$ (M)**	**τ_{Δ} (μs)**	**k_d (s^{-1})**	**k_t^{PS} ($M^{-1}s^{-1}$)**
Cyclohexane	8.7×10^{-5}	27	3.70×10^{4}	4.3×10^{7}
Toluene	4.5×10^{-5}	27	3.70×10^{4}	8.2×10^{7}
Dioxane	7.4×10^{-5}	30	3.33×10^{4}	4.5×10^{7}
Chloroform	3.8×10^{-5}	201	4.98×10^{3}	1.3×10^{7}
Dichloromethane	6.5×10^{-5}	97	1.03×10^{4}	1.6×10^{7}
Acetone	3.8×10^{-5}	58	1.72×10^{4}	4.5×10^{7}
Acetonitrile	4.5×10^{-5}	81	1.23×10^{4}	2.7×10^{7}
EtOH	5.9×10^{-5}	18	5.56×10^{4}	9.4×10^{7}
MeOD	7.1×10^{-5}	37	2.70×10^{4}	3.8×10^{7}
MeOH	8.8×10^{-5}	10	9.09×10^{4}	1.1×10^{8}
D_2O:MeOD (1:1)	7.2×10^{-5}	45	2.22×10^{4}	3.8×10^{7}

Table S4: Result of triplet lifetime (τ_{obs}^{T}), λ_{ex}= 570 nm, λ_{em}=425 nm after degassing by nitrogen for 10 minutes.

Solution	**Concentration β-Carotene (M)**	**τ_{obs}^{T} (ns)**	**$1/\tau_{obs}^{T}$ (ns^{-1})**
A	0	34300	2.9×10^{-5}
B	8.2×10^{-7}	22000	4.5×10^{-5}
C	2.4×10^{-6}	17500	5.7×10^{-5}
D	2.5×10^{-6}	15100	6.6×10^{-5}
E	4.1×10^{-6}	13200	7.6×10^{-5}
F	7.2×10^{-6}	11000	9.1×10^{-5}
G	8.2×10^{-6}	8100	1.2×10^{-4}
H	1.2×10^{-5}	6500	1.5×10^{-4}
I	1.6×10^{-5}	4100	2.4×10^{-4}
J	2.4×10^{-5}	3000	3.3×10^{-4}

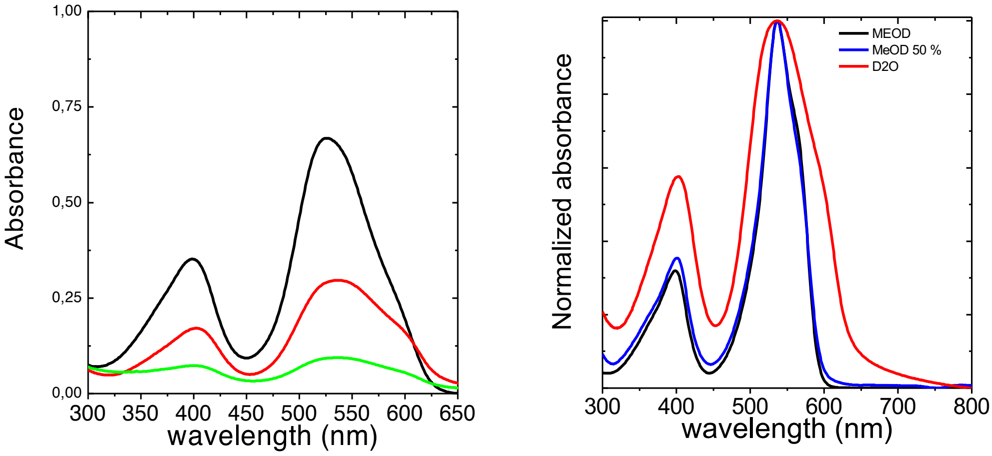

Figure S1: Left: absorption spectra of MeSBDP in D_2O (5.6×10^{-6} M (green), 1.8×10^{-5} M (red) and 3.5×10^{-5} M (black); Right: Normalized absorption spectra of different solutions of MeSBDP in MeOD (black), D_2O (red) and MeOD/D_2O 50/50% (blue).

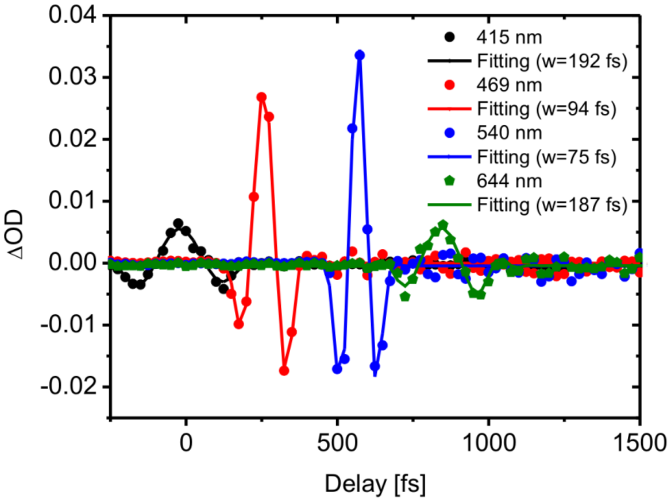

Figure S2. IRF at selected probe wavelengths measured in chloroform. The amplitude of the transient at 644 nm has been multiplied by a factor 2 to improve its visibility.

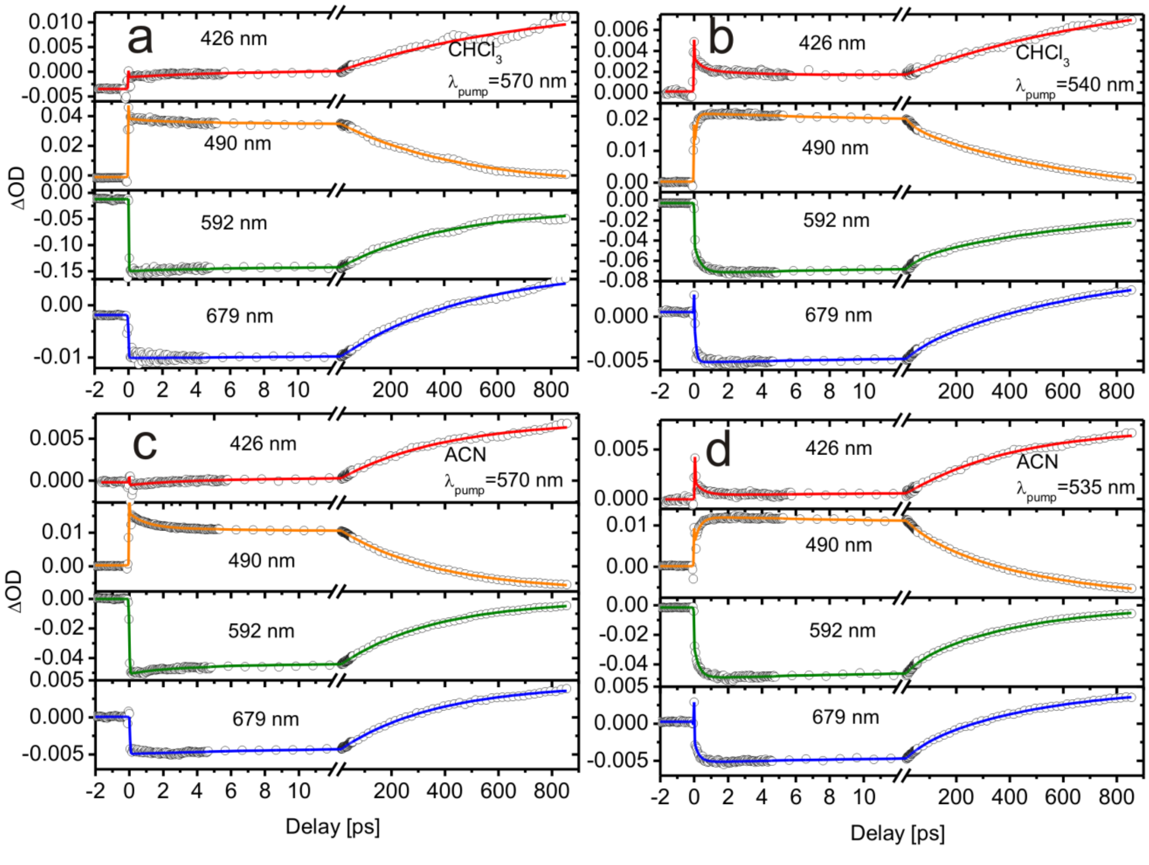

Figure S3: Temporal evolution of the main fs-TA bands of MeSBDP in chloroform (a,b) and acetonitrile (c,d) resulting from excitation at the indicated wavelength. Solid lines represent the fitting with a multiexponential decay convoluted with the instrumental response funtion (~100 fs) . Each data set is shown together with the corresponding multiexponential fit. In any case, a triexponential fit with time constants τ_1~1 ps, τ_2~500 ps and τ_3>>1 ns was introduced, except for the results corresponding to excitation at higher energies (540 nm for $CHCl_3$ and 535 nm for CH_3CN), which required an additional decay (τ_2~70 ps) to satisfactorily reproduce the experimental data.

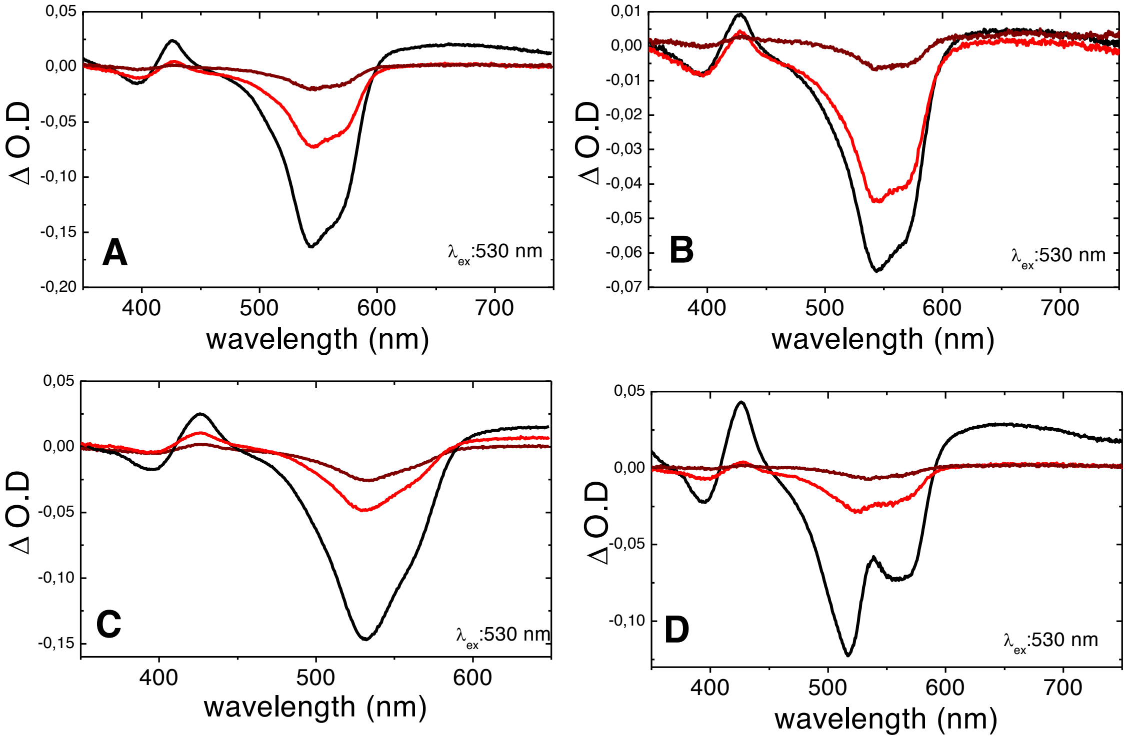

Figure S4: ns-transient absorption spectra recorded during 1 microsecond in air-saturated (red), nitrogen-saturated (black) and oxygen-saturated (brown) in toluene (A) chloroform (B), acetonitrile (C) and methanol (D). λ_{ex}*=530 nm*

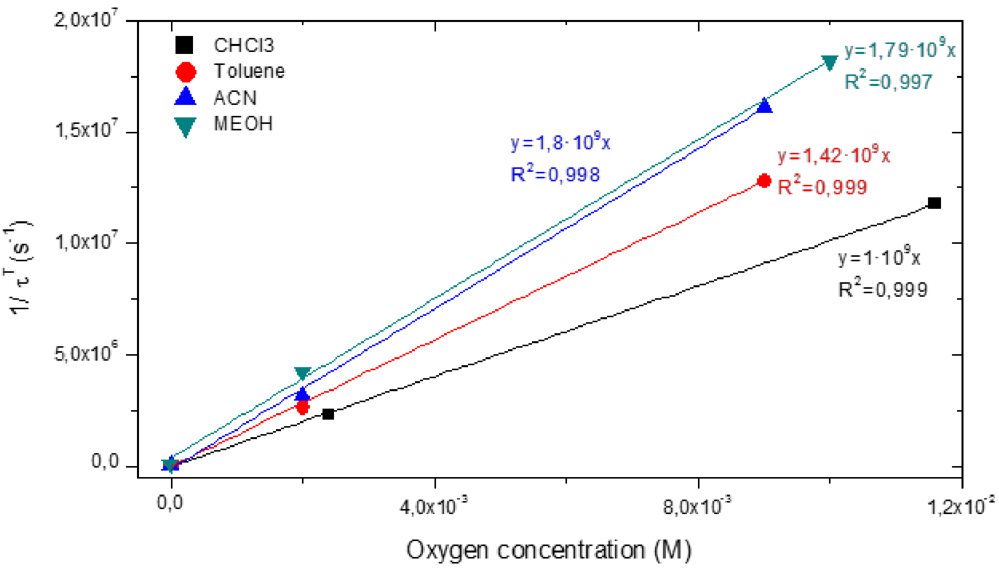

Figure S5: Determination of the bimolecular rate constants of triplet quenching of MeSBDP by molecular oxygen (k^{T}_{q,O_2}*) at room temperature in CHCl*$_3$ *(black square), toluene (red circle), acetonitrile (blue triangle) and methanol (green triangle).*

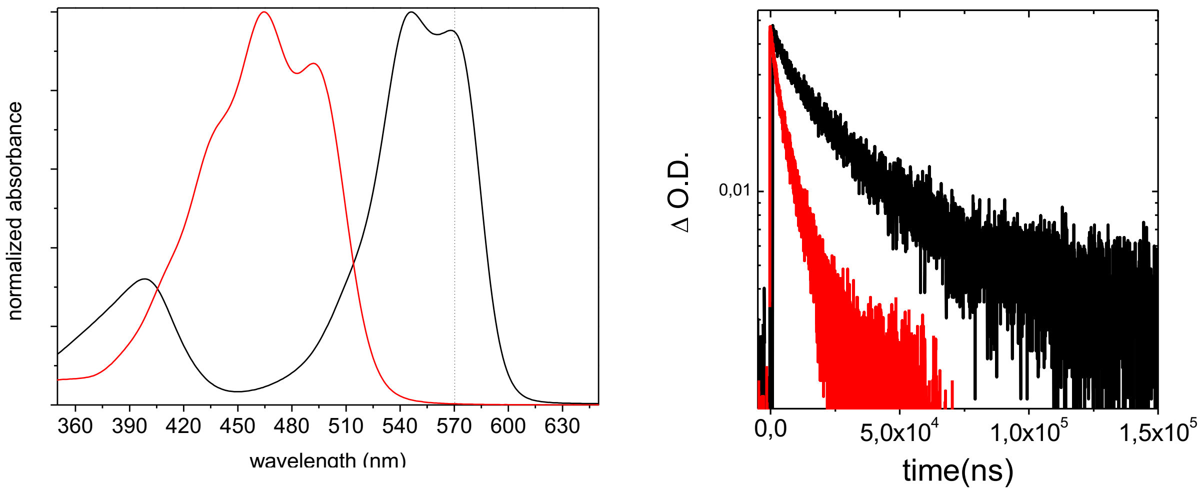

Figure S6: Left) Normalized absorption spectra of MeSBDP (black) and of the triplet acceptor β-carotene (red) in chloroform. Right) Decay curves of triplet ^{3}MeSBDP in the absence of β-carotene (black curve) and in the presence of β-carotene at $4.1x10^{-6}$ M (red curve), recorded at 425 nm under λ_{ex} 570 nm in N_2 degassed chloroform solutions.*

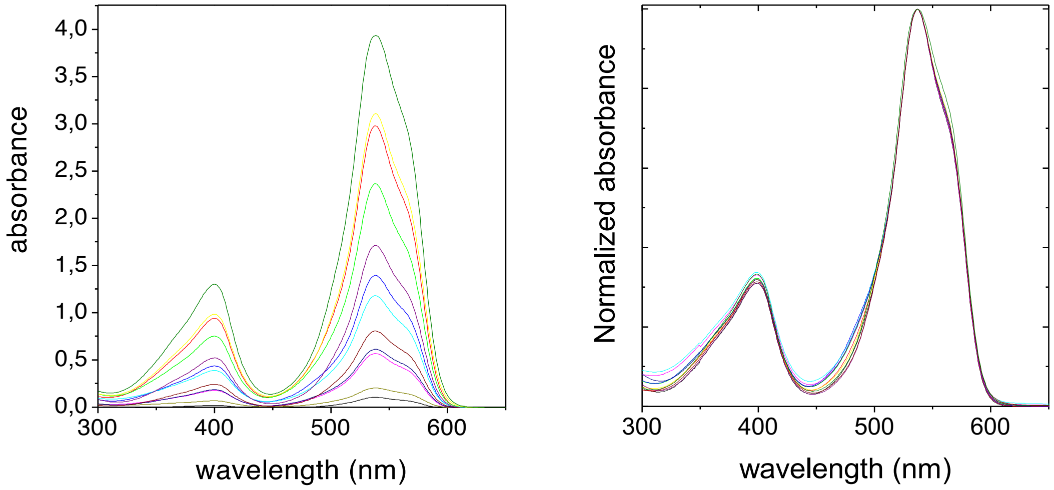

Figure S7:. Left) Absorption spectra of MeSBDP in MeOH at different concentration between $2.6x10^{-6}$ to $8.8x10^{-5}$ M; Right) Normalized absorption spectra

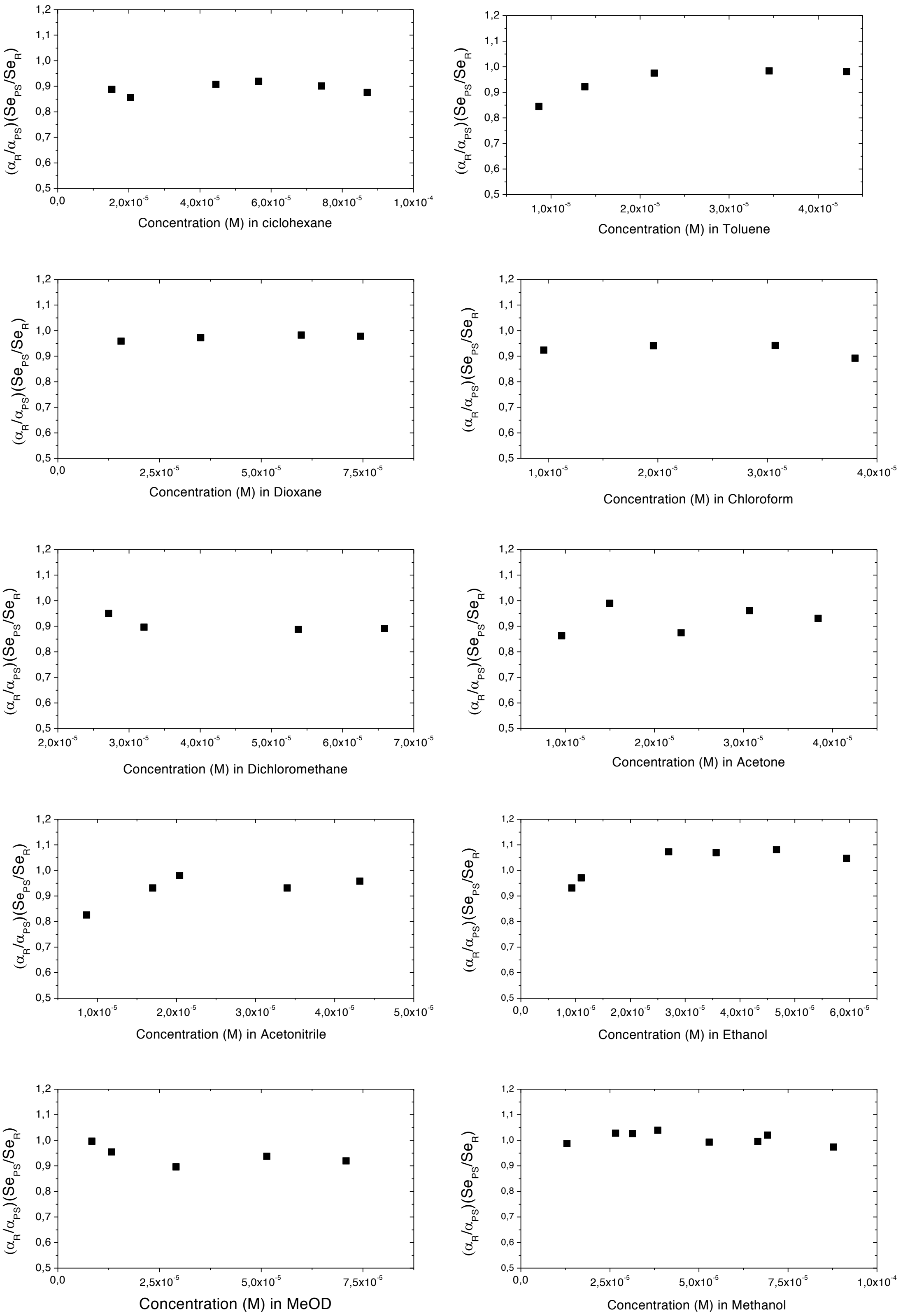

Figure S8: Variation of the ratio $(S_{0,PS_{Ref}}/S_{0,PS})(\alpha_{PS}/\alpha_{PS_{Ref}})$ of singlet oxygen emission signal for MeSBDP as a function of MeSBDP concentration in representative solvents at room temperature. Error: approx. 10%

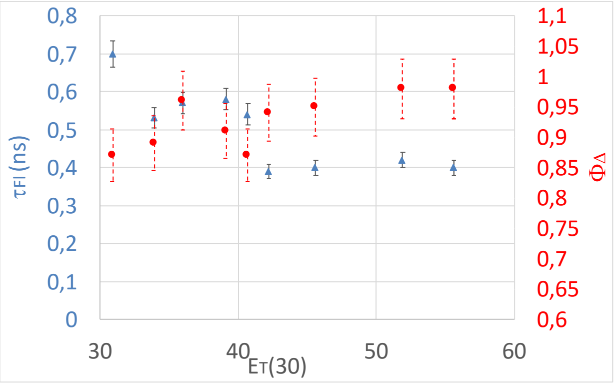

Figure S9: Evolution of fluorescence lifetime and singlet oxygen quantum yield with the solvent polarity

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