

Supporting information

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General information

Materials. All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. CH_2Cl_2 was obtained from Fisher Scientific.

Toluene was obtained from Sigma-Aldrich (Lab. Reagent grade, 99.3%) and was dried and purified carefully to remove fluorescent impurities and potentially coordinating species.^[1] Methylthiophenes and other sulfur containing impurities and petroleum side products were removed from toluene (1000 mL) through shaking it with concentrated sulfuric acid (200 mL). The separated organic phase was washed with first water 400 (mL), then by 10% aq. solution of sodium hydroxide (200 mL) and again by water (400 mL). Toluene was pre-dried over MgSO_4 and filtered. The resulted toluene was distilled under nitrogen atmosphere from the sodium as a drying agent. All solvents were stored over molecular sieves (4 Å) under N_2 . $[\text{IrCl}(\text{cod})(\text{NHC})]$ complexes used in this work were synthesized according to known literature procedures.^{[2][3]} bdpSO_3Ag and corresponding $\text{Ir}(\text{bdpSO}_3)(\text{cod})(\text{NHC})$ were synthesized according to the reported procedure.^[3]

Instrumentation. UV-Vis spectra were recorded on Analytik Jena Specord 600 UV-Vis spectrometer, fluorescence spectra were recorded on J&M TIDAS S700/CCD UV/NIR 2098 spectrometer combined with J&M TIDAS LSM monochromator with 75 W Xenon light source and thermo-controlled cuvette holder. Samples for emission and absorption measurements were contained in 1 cm quartz cuvette (Hellma Analytics). The photoreactions were performed using a green LED light strip (12 V strip green light 5 m 3528 SMD 300 LED, 60 LED/m, 4.8 W per metre strips). Home-built photoreactor was made by wrapping approximately 2.3 m (11.0 W) of the LED strips around a 600 ml glass beaker and corresponding setup was kept unchanged during all measurements. The quartz cuvettes were placed in the middle of the photoreactor, with an estimated bottom diameter 9 cm and centre diameter 8.4 cm for the beaker reactor. Dynamic light scattering experiments (DLS) were performed with a Malvern Zetasizer Nano ZS, with a sensitivity ranging from 0.3 to 10000 nm.



Figure S 1 Home-built photoreactor for photo catalytic experiments.

General Procedures

General procedure for the singlet oxygen experiments. A mixture of 1,3-diphenylisobenzofuran (DPBF) (90 μM) and the respective photocatalyst (1.0 μM) was dissolved in the corresponding solvent (2 mL) and irradiated under green LED light ($\lambda_{\text{max}} = 510$ nm) in a home-built photoreactor (figure S1). The photooxidation of DPBF was monitored over time, ranging from 5 seconds to 2 minutes, depending on the efficiency of the photocatalyst. The time-dependent absorption graphs show the decrease in the DPBF signal at 410 nm and the corresponding linear regression from which the rate constant was calculated.

The Φ_{Δ} data was obtained using 2,6-diiodobodipy ($\Phi_{\Delta} = 0.94$ in toluene) as the reference^[5]:

$$\Phi_{\Delta} = \Phi_{\Delta}^{st} \frac{r}{r^{st}} \frac{I^{st}}{I}$$

where (r) and (r^{st}) are the DPBF photooxidation rate constants in the presence of the corresponding photocatalyst (calculated from the decrease in absorbance at 410 nm), respectively; (I) and (I^{st}) are relative absorbance correction factors and were calculated according to the spectrum of the light source and the absorbance spectrum of the photosensitizer. Relative absorbance (I) allows translation of the experimental data from photosensitizers with different absorbance spectrums using a non-monochromatic light source for the irradiation.

$$I = \int_{484}^{600} i(\lambda) (1 - 10^{-A(\lambda)}) d(\lambda)$$

Where the integral of i , is the intensity of the light source at the specific wavelength (λ), with the corresponding absorbance value (A) at the given wavelength (λ)^[4].

General procedure for the fluorescence experiments. All experiments were carried out in quartz cuvettes with path lengths of 10.0 mm. A cuvette was charged with 2000 μL of 1.0 μM solution of the respective $[\text{Ir}(\text{bdpSO}_3)(\text{cod})(\text{NHC})]$ complex in toluene. The temperature ($T = 25\text{ }^\circ\text{C}$) was adjusted using a thermostat. Portions of DMSO in ion separation experiment were added to the cuvette in fixed amounts of 2 – 10 μL . For the fluorescence quenching experiment 0.2 *mM* $\text{NBu}_4\text{Br} / \text{NaBAr}_4^{\text{F}}$ salt solutions in 1,2-dichloroethane were added to the cuvette (typical range 5 μL - 50 μL). After each aliquot, the fluorescence intensity was monitored. The next aliquot was added when the fluorescence level was found to remain constant, which is typically the case after 30 s of light exposure. The titration was terminated when addition of a new aliquot did not lead to a further increase in the fluorescence. The fluorescence data were finally corrected for dilution of the sample. In order to avoid mistakes in the preparation of solution of photocatalyst each fluorescence value of the 1.0 μM solution of the respective $[\text{Ir}(\text{bdpSO}_3)(\text{cod})(\text{NHC})]$ complex in toluene were monitored prior to the photooxidation experiment. Following the photooxidation experiment of DPBF to obtain the respective fluorescence intensity for the fully separated ion pair, an 8 M solution of NBu_4Br in 1,2-dichloroethane was added (10 μL , $8.00 \cdot 10^{-5}$ mol, 40000 eq).

Complexes studied

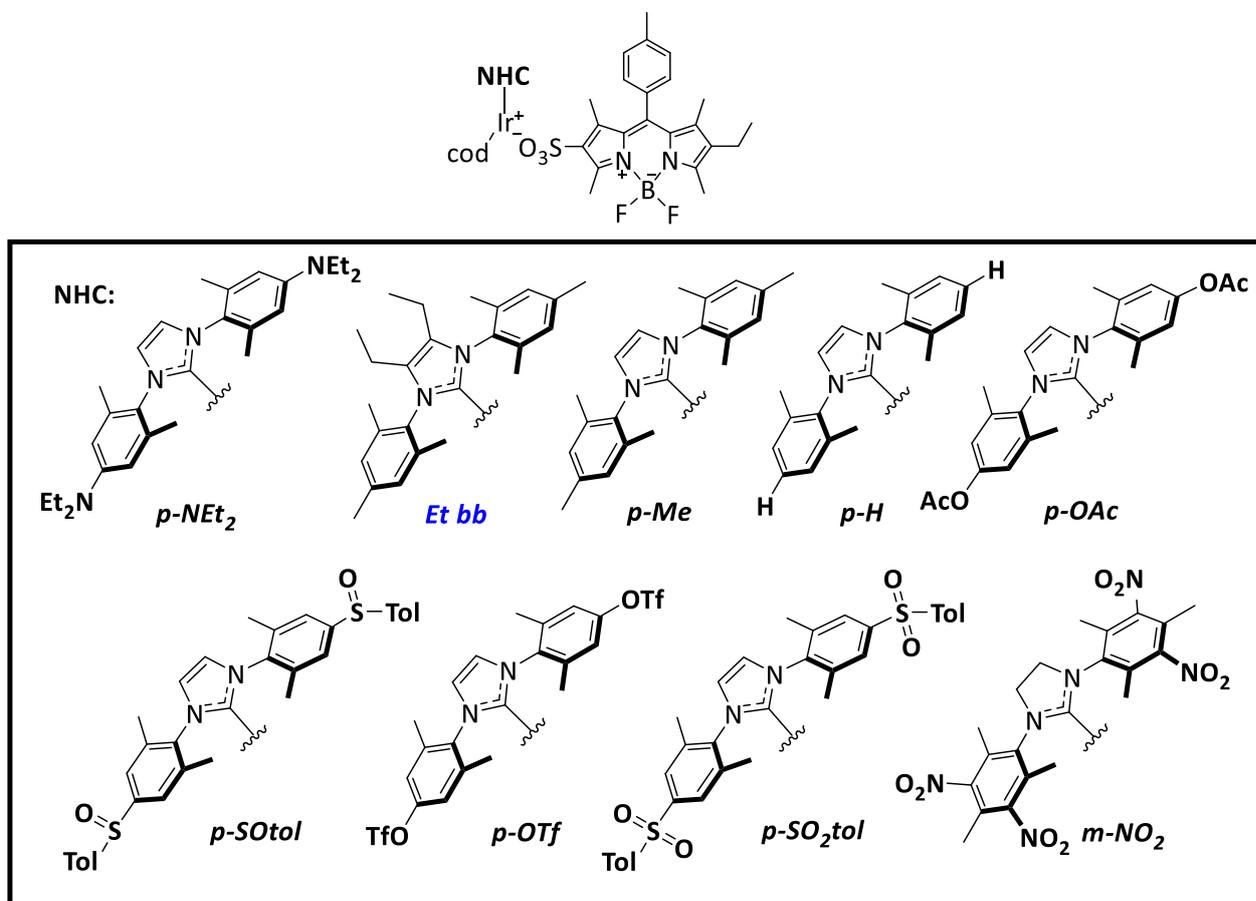


Figure S 2 [Ir(bdpSO₃)(cod)(NHC)] complexes studied in ¹O₂ generation.

UV/Vis and fluorescence data

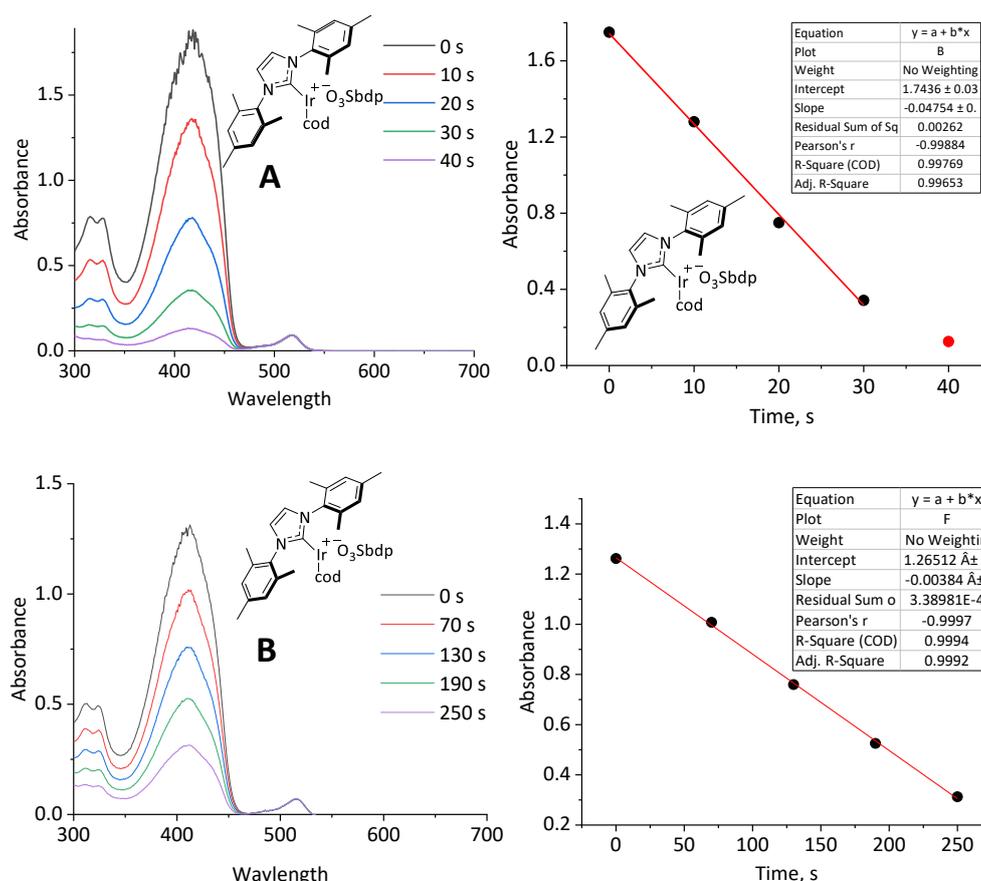


Figure S 3 Left: **A**: Decay of the DPBF in the absorption spectra ($c_0 = 90 \mu\text{M}$) in a presence of $[\text{Ir}(\text{bdpSO}_3)(\text{cod})(\text{IMes})]$ ($c = 1.0 \mu\text{M}$) in toluene solution. **B**: Decay of the DPBF ($c_0 = 90 \mu\text{M}$) in a presence of $[\text{Ir}(\text{bdpSO}_3)(\text{cod})(\text{IMes})]$ ($c = 1.0 \mu\text{M}$) in CH_3CN solution. Solutions were irradiated with a green LED ($\lambda_{\text{max}} = 510 \text{ nm}$). Right: Linear regression for decrease of the absorbance of DPBF at 410 nm for **A** and **B**.

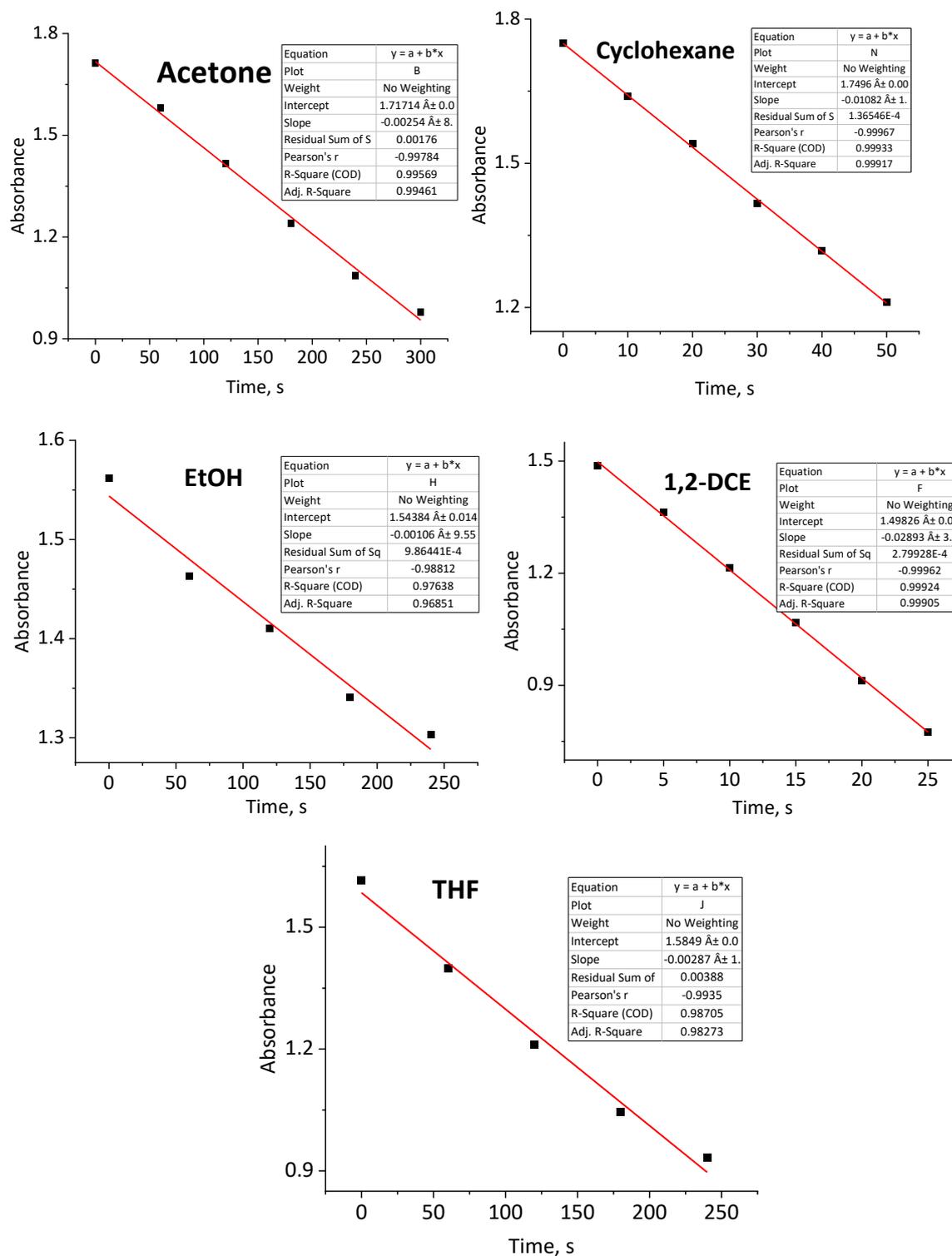


Figure S 4 Represents corresponding linear regression for decrease of the absorbance of DPBF ($C_0 = 90 \mu\text{M}$) at 410 nm for $[\text{Ir}(\text{bdpSO}_3)(\text{cod})(\text{IMes})]$ complex ($c = 1.0 \mu\text{M}$) in different solvent solutions. Solutions were irradiated with a green LED ($\lambda_{\text{max}} = 510 \text{ nm}$).

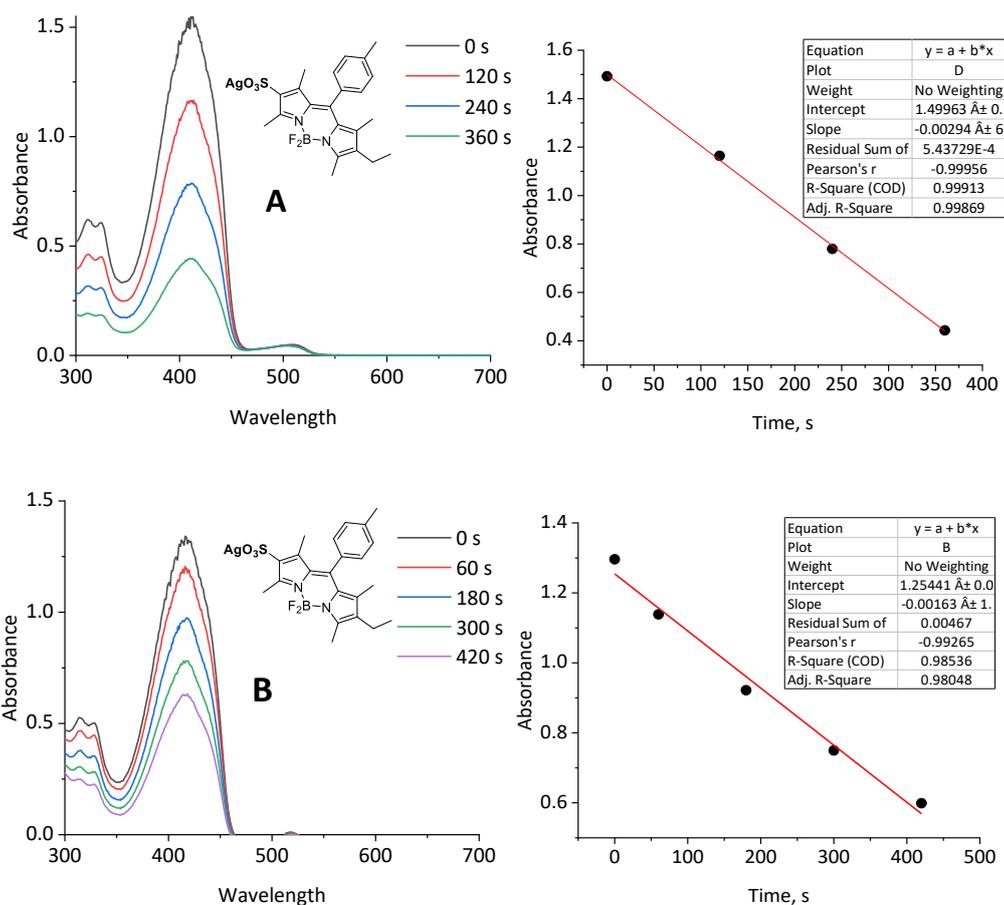


Figure S 5 Left: **A**: Decay of the DPBF in the absorption spectra ($c_0 = 90 \mu\text{M}$) in a presence of bdpSO_3Ag ($c = 1.0 \mu\text{M}$) in CH_3CN solution. **B**: Decay of the DPBF ($c_0 = 90 \mu\text{M}$) in a presence of bdpSO_3Ag ($c = 1.0 \mu\text{M}$) in toluene solution. Solutions were irradiated with a green LED ($\lambda_{\text{max}} = 510 \text{ nm}$). Right: Linear regression for decrease of the absorbance of DPBF at 410 nm for **A** and **B**.

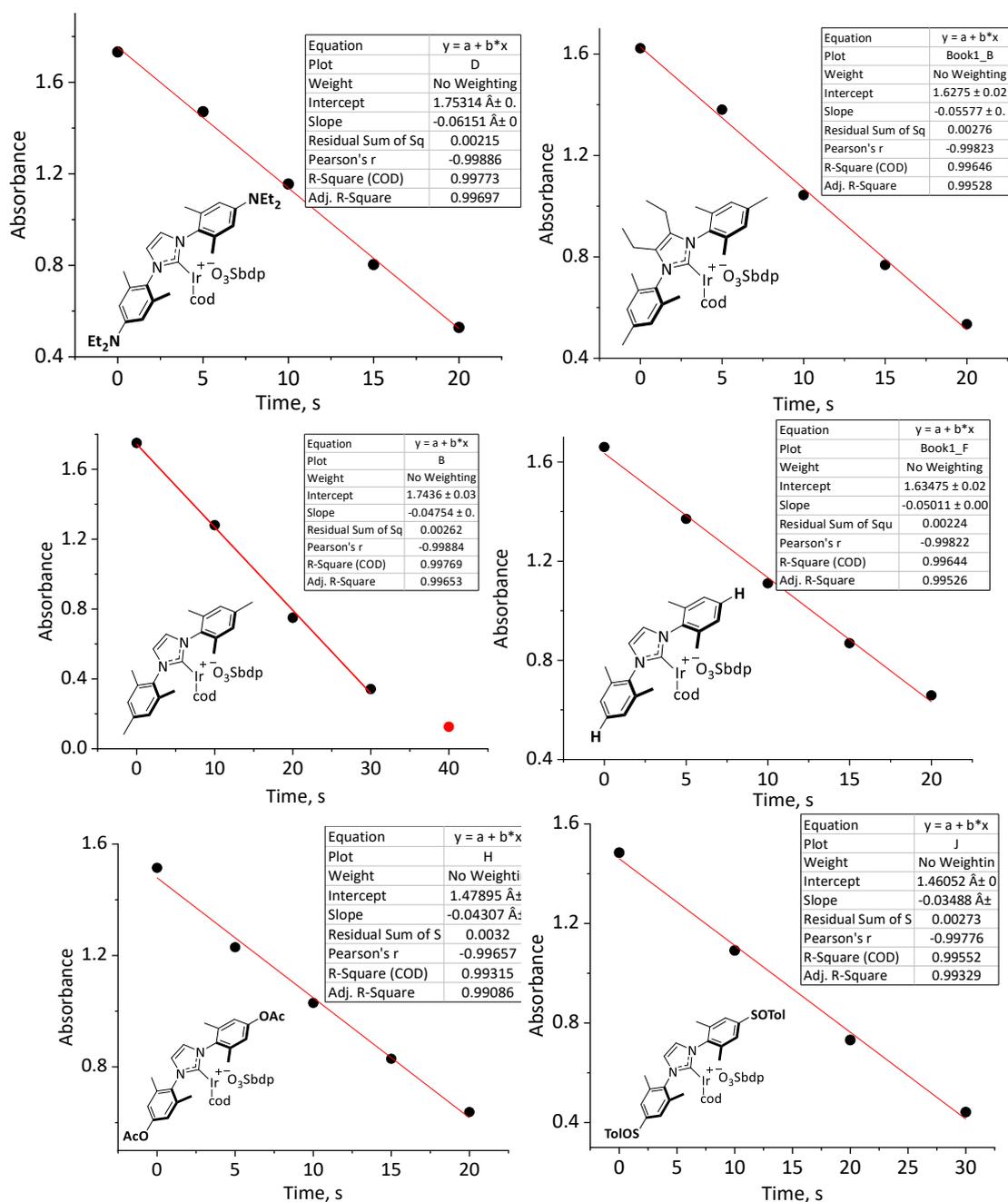


Figure S 6 Represents corresponding linear regression for decrease of the absorbance of DPBF ($c_0 = 90 \mu\text{M}$) at 410 nm for different NHC ligands in [Ir(bdpSO₃)(cod)(NHC)] complexes ($c = 1.0 \mu\text{M}$) in toluene solution. Solutions were irradiated with a green LED ($\lambda_{\text{max}} = 510 \text{ nm}$).

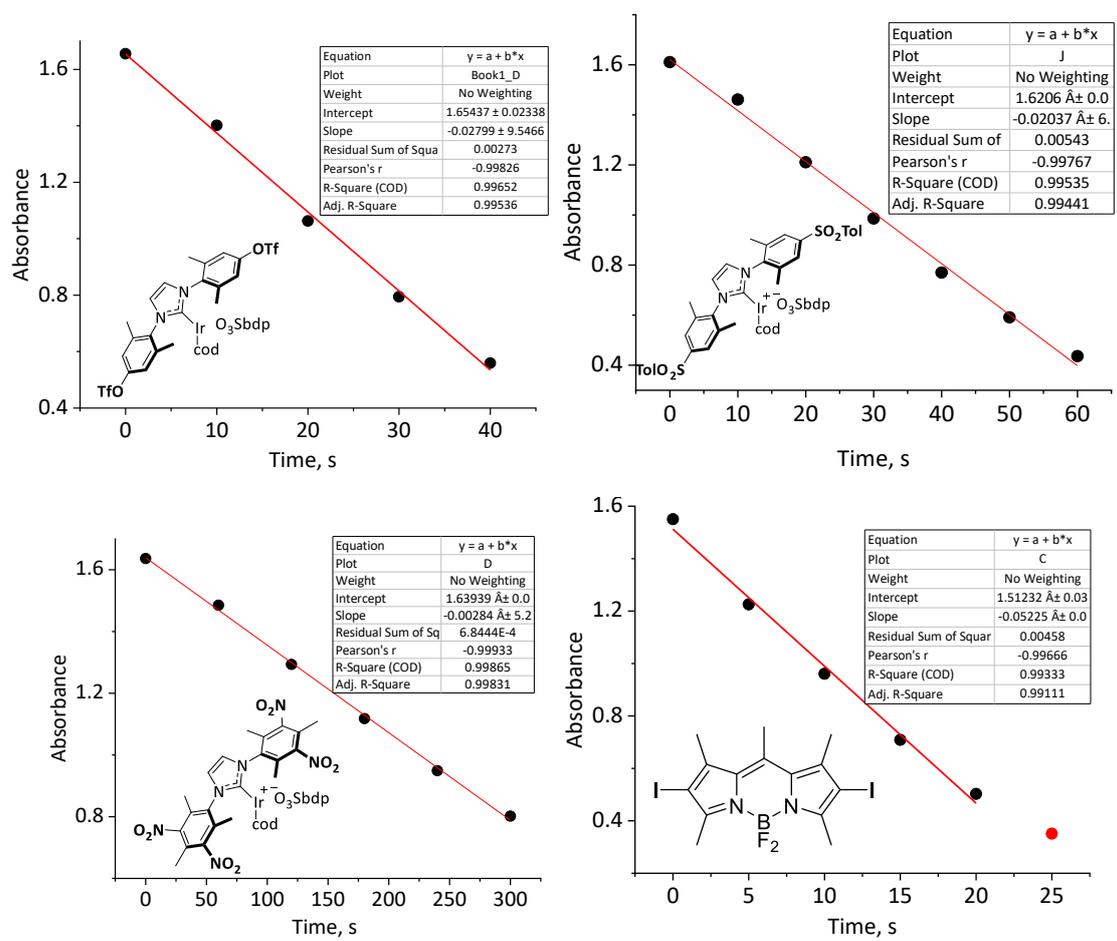


Figure S 7 Representation of corresponding linear regression for decrease of the absorbance of DPBF ($c_0 = 90 \mu\text{M}$) at 410 nm for different photocatalysts ($c = 1.0 \mu\text{M}$) in toluene solution. Solutions were irradiated with a green LED ($\lambda_{\text{max}} = 510 \text{ nm}$).

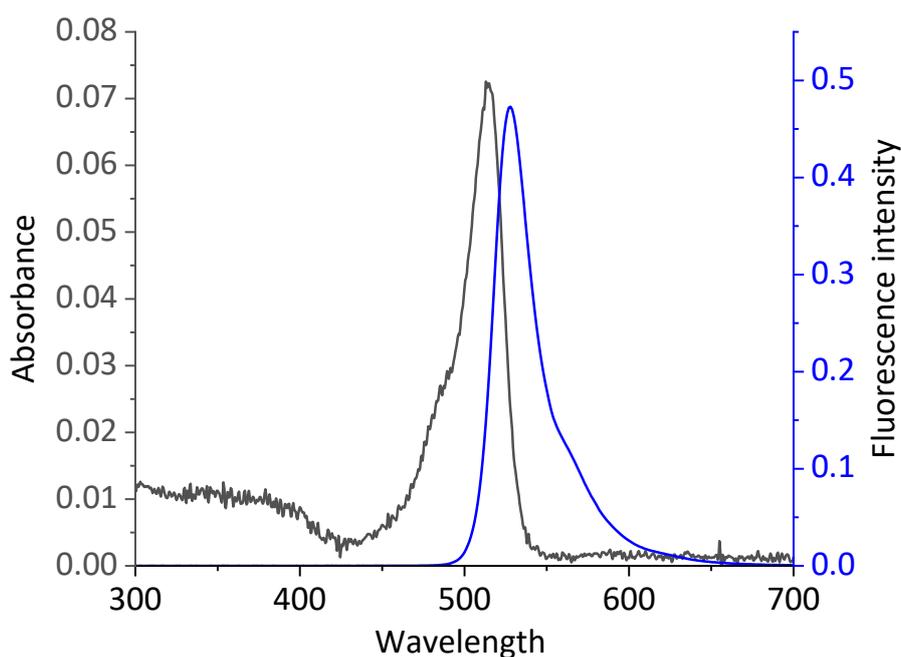


Figure S 8 Absorbance (black, $\lambda_{\text{abs, max}} = 516 \text{ nm}$) and emission $\lambda_{\text{exc}} 516 \text{ nm}$ (blue, $\lambda_{\text{em, max}} = 527 \text{ nm}$) spectra of $1.0 \mu\text{M}$ solution of bdpSO_3Ag in 1,2-dichloroethane.

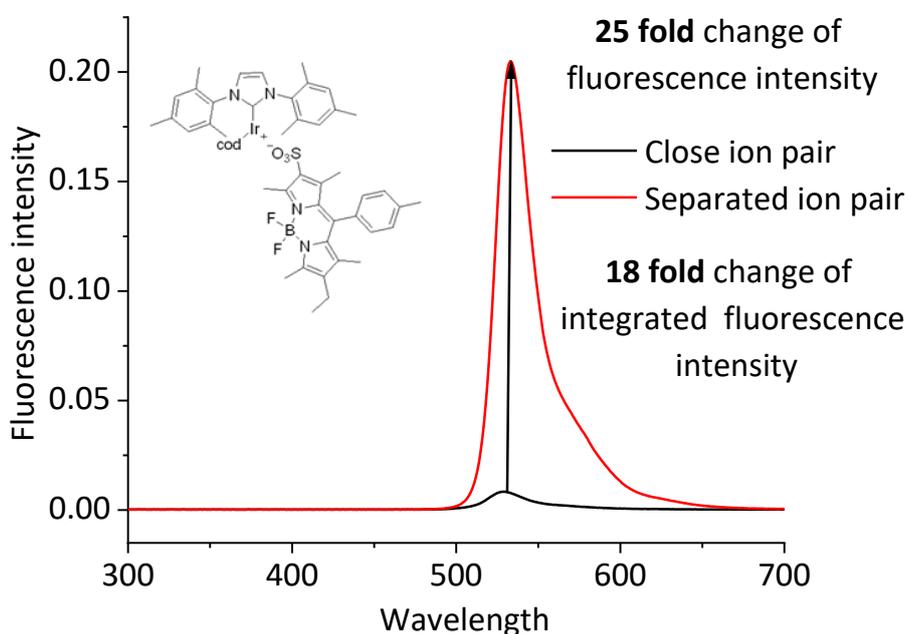


Figure S 9 Fluorescence spectra ($\lambda_{\text{exc}} = 516 \text{ nm}$) of close ion paired complex $[\text{Ir}(\text{bdpSO}_3)(\text{cod})(\text{IMes})]$ ($c = 1.0 \mu\text{M}$) in toluene solution (**black**) and separated ion paired complex in toluene solution after addition of NBu_4Br (**red**).

Correlation of redox potentials and singlet oxygen generation data

<i>Photocatalyst</i>	$\Delta E_{1/2}$ [V] ^[3]	$k(po)$	$\Phi_{\Delta}(^1O_2)$
<i>(p-NEt₂)</i>	0.648	0.062	0.88
<i>(Et bb)</i>	0.681	0.056	0.86
<i>(p-Me)</i>	0.765	0.048	0.76
<i>(p-H)</i>	0.786	0.050	0.73
<i>(p-OAc)</i>	0.793	0.043	0.69
<i>(p-SOTol)</i>	0.870	0.035	0.55
<i>(p-OTf)</i>	0.903	0.028	0.44
<i>(p-SO₂Tol)</i>	0.920	0.020	0.37
<i>(m-NO₂)</i>	1.045	0.003	0.05
<i>(bdpSO₃Ag)</i>	-	0.002	0.01
<i>(2,6-diiodobdp)</i>	-	0.052	0.94

Table S 1 Redox potentials of various photocatalysts (1,2-dichloroethane/NBu₄PF₆ (0.1 M)).^[3] Rate $k(po)$ of ¹O₂ generation by different photocatalysts catalysts in photooxidation reaction of DPBF ($c_0 = 90 \mu\text{M}$) in toluene solution ($c = 1.0 \mu\text{M}$). $\Phi_{\Delta}(^1O_2)$ singlet oxygen quantum yield.

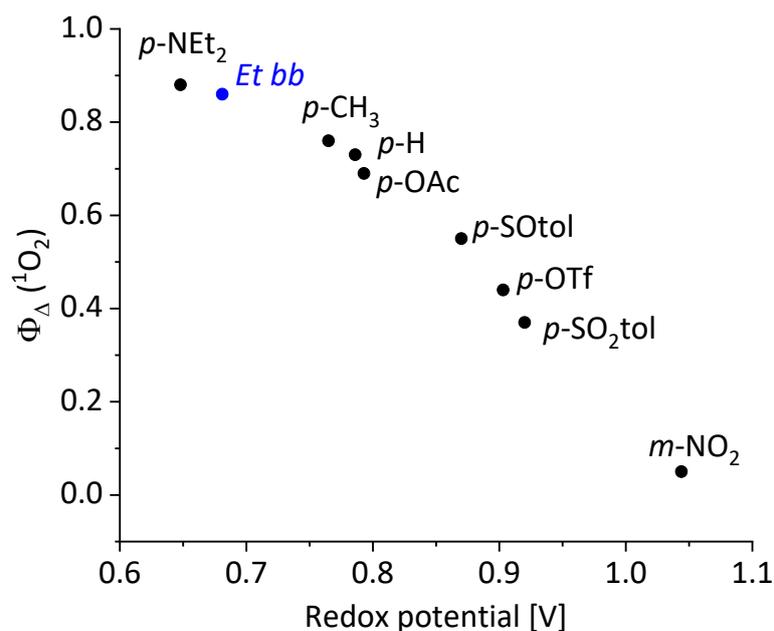


Figure S 10 $\Phi_{\Delta}({}^1\text{O}_2)$ singlet oxygen quantum yield generated by [Ir(bdpSO₃)(cod)(NHC)] complexes in toluene solution ($c = 1.0 \mu\text{M}$) vs. redox potential plot for [IrCl(cod)(NHC)] complexes in 1,2-dichloroethane.

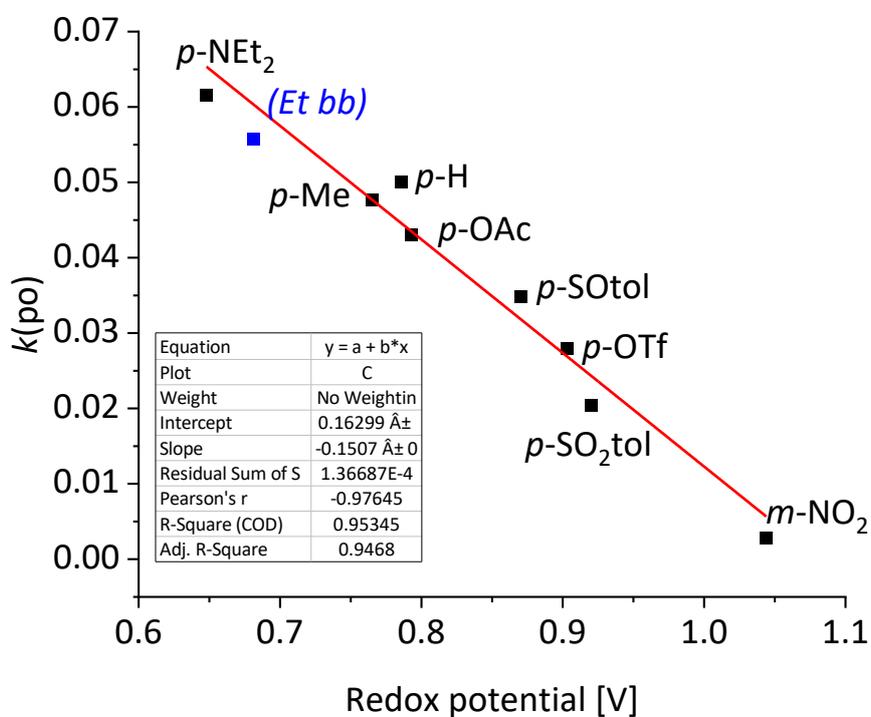


Figure S 11 Rate $k(\text{po})$ of ${}^1\text{O}_2$ generation by [Ir(bdpSO₃)(cod)(NHC)] complexes in toluene solution ($c = 1.0 \mu\text{M}$) vs. redox potential plot for [IrCl(cod)(NHC)] complexes in 1,2-dichloroethane.

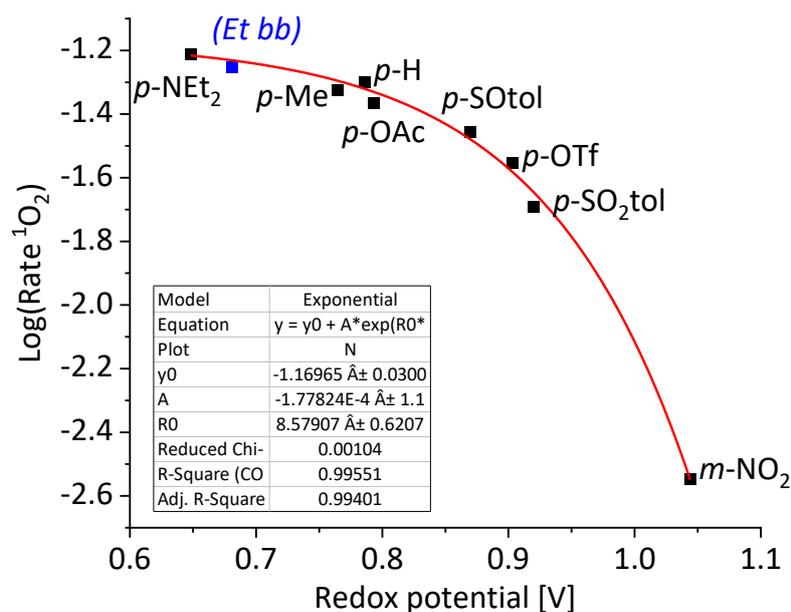


Figure S 12 Log(Rate) of $^1\text{O}_2$ generation by $[\text{Ir}(\text{bdpSO}_3)(\text{cod})(\text{NHC})]$ complexes in toluene solution ($c = 1.0 \mu\text{M}$) vs. redox potential plot for $[\text{IrCl}(\text{cod})(\text{NHC})]$ complexes in 1,2-dichloroethane.

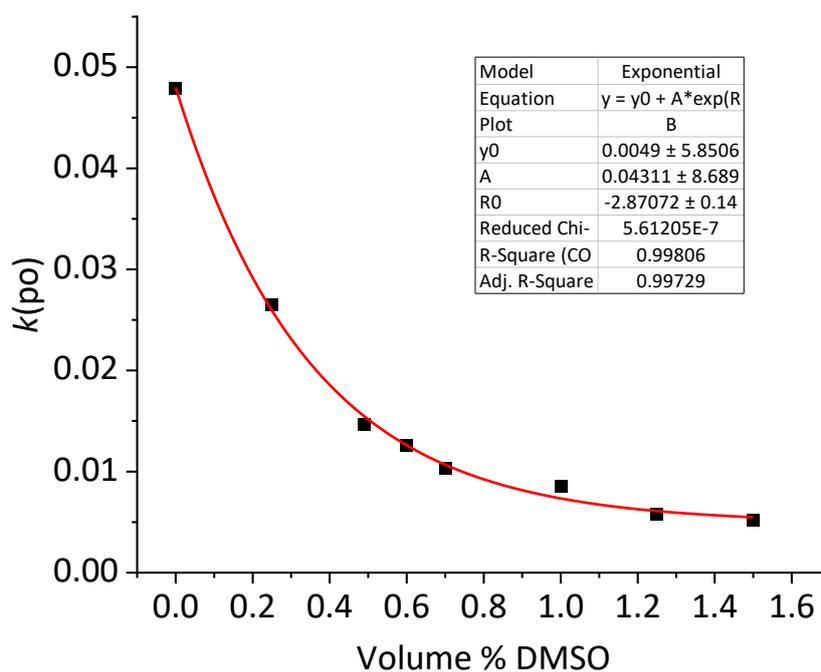


Figure S 13 Rate $k(\text{po})$ of $^1\text{O}_2$ generation by $[\text{Ir}(\text{bdpSO}_3)(\text{cod})(\text{IMes})]$ complex in toluene solution ($c = 1.0 \mu\text{M}$) followed by addition of DMSO.

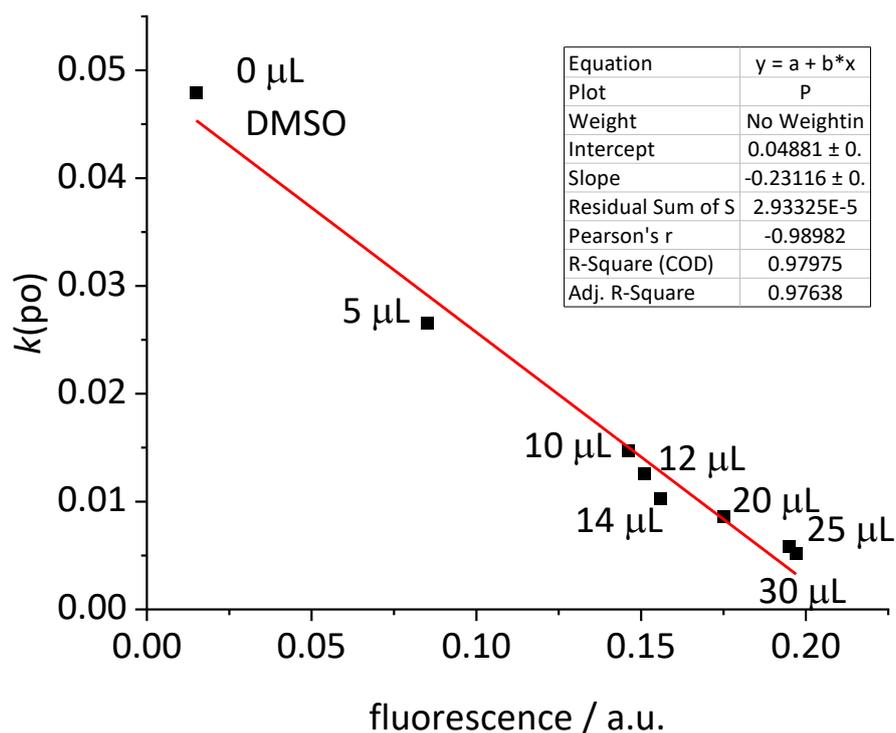


Figure S 14 Rate $k(\text{po})$ of $^1\text{O}_2$ generation by $[\text{Ir}(\text{bdpSO}_3)(\text{cod})(\text{IMes})]$ complex in toluene solution ($c = 1.0 \mu\text{M}$) vs. Change of fluorescence intensity after addition of DMSO to the solution of complex in toluene.

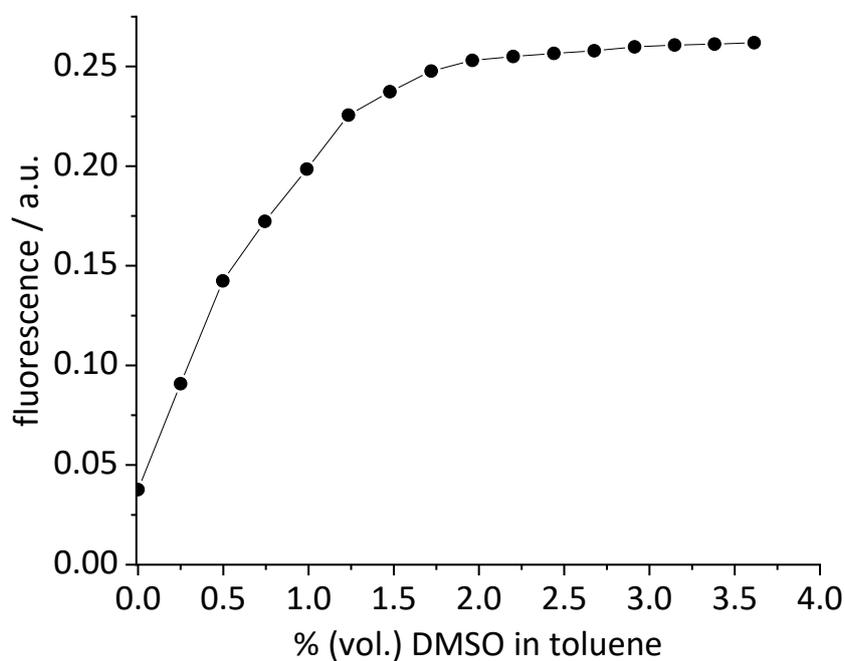


Figure S 15 Change of fluorescence intensity for $[\text{Ir}(\text{bdpSO}_3)(\text{cod})(\text{IMes})]$ complex ($c = 1.0 \mu\text{M}$) in toluene solution followed by addition of DMSO.

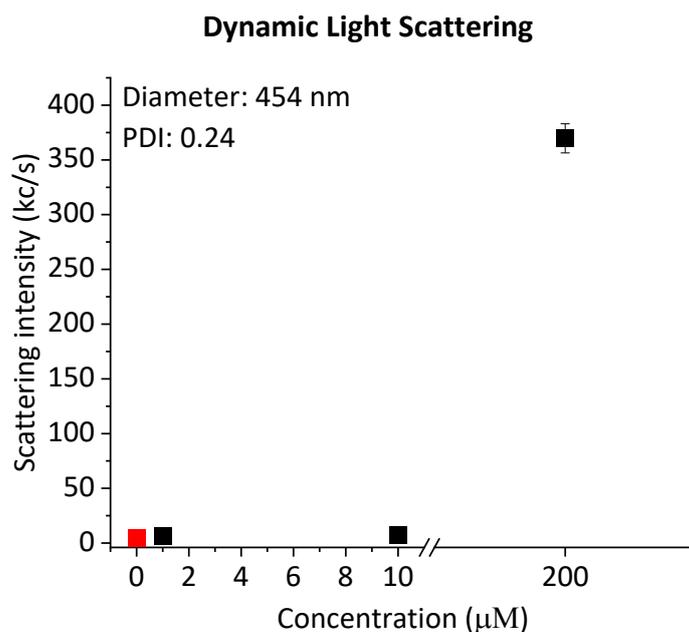


Figure S 16 Scattering intensity (kc/s) measured for $[\text{Ir}(\text{bdpSO}_3)(\text{cod})(\text{IMes})]$ complex at different concentrations in toluene solution.

Method: Samples at different concentrations (0, 1, 10 and 200 μM) were measured with a Malvern Zetasizer Nano ZS, with a sensitivity ranging from 0.3 to 10000 nm. The results were measured in a disposable plastic cuvette (10 measurements in 10 seconds). The laser position was fixed at 4.65 mm, and the attenuator was fixed at 11 mm (ensuring highest laser intensity). The results were analyzed with the Malvern Zetasizer software, which allows the fitting of a meaningful result with a signal above 200 kc/s. Results are displayed as mean \pm SD (n=3).

Description: As the scattered light intensity is directly proportional the concentration of the analyte, by keeping the laser power constant, the derived signal can be related to the amount of scattering species in the sample. The signal of pure toluene (red square) is roughly the same as that of the two lower concentrations (1 μM and 10 μM), meaning that the complex doesn't detectably aggregate. At 200 μM , however, the intensity is 60 times higher and falls in the 200-500 kc/s range. Software is able to fit it to a cumulant analysis, showing particles with an average of 450 nm diameter and a broad polydispersity index (PDI).

DLS is not able to directly count the number of particles but, having obtained this intensity using the maximum laser power, points to a limited degree of aggregation.

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- [2] T. Vorfalt, S. Leuthäuser, H. Plenio, *Angew. Chem., Int. Ed.*, **2009**, *48*, 5191.
- [3] S. Popov, H. Plenio, *Eur. J. Inorg. Chem.*, **2021**, 3708 –3718.
- [4] L. V. Lutkus, S. S. Rickenbach, T. M. McCormick, *J. Photochem. Photobiol. A.*, **2019**, *378*, 131–135.
- [5] A. Buglak, A. Charisiadis, A. Sheehan, C. Kingsbury, M. Senge, M. Filatov, *Chem. Eur. J.*, **2021**, *27*, 9934 – 9947.