

Supporting Information

DABCONium: An Efficient and High-Voltage Stable Singlet Oxygen Quencher for Metal–O₂ Cells

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Experimental Procedures

Materials

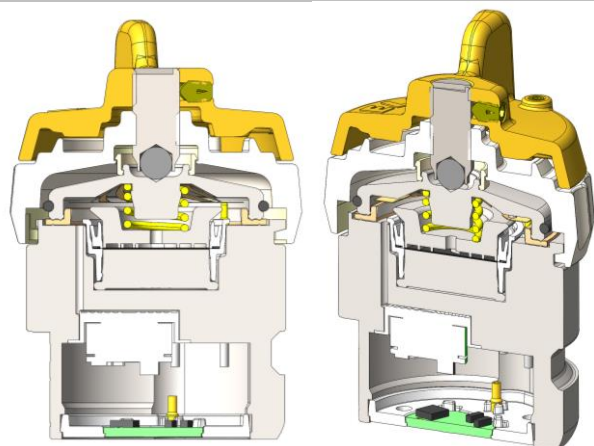
All chemicals were purchased from ABCR Chemicals, Fluka, Merck, Sigma Aldrich, Solvionic, VWR Chemicals. They were used without further purification unless noted. Dry dichloromethane (DCM) was produced by heating refluxing it for 12 h over P₄O₁₀ under inert atmosphere and afterwards distilling it into a Schlenk flask. Dry tetrahydrofuran (THF) was made by passing it over an aluminum oxide column. LiTFSI was dried under vacuum for 24 h at 80 °C. Dimethoxyethane (DME) and tetraethylene glycol dimethyl ether (TEGDME) were dried over lithium, distilled and further dried and stored over activated molecular sieves. The water content was determined by Karl-Fisher titration and found to be below 5 ppm. 9,10-Dimethylanthracene (DMA) was recrystallized from ethanol and its purity confirmed by ¹H-NMR spectroscopy and HPLC analysis. 1,4-diazabicyclo[2.2.2]octane (DABCO) was from Sigma-Aldrich and was recrystallized from absolute diethyl ether. The sensitizer palladium(II) *meso*-tetra(4-fluorophenyl)tetrabenzoporphyrin (Pd₄F) was synthesized according a previously reported procedure.^[1] Lithium iron phosphate (LFP) was partially delithiated according to a previously reported procedure.^[2]

Electrode fabrication

Carbon cathodes were made by first making a slurry of carbon with PTFE binder (suspension of 60% w/w in H₂O, Aldrich) in the ratio 9:1 (m/m) using isopropanol. The slurry was then coated onto a stainless steel mesh current collector. The electrodes were vacuum dried at 200 °C for 24 h and then transferred to an Ar filled glove box without exposure to air. The glass fiber separators were washed with ethanol and dried overnight at 200 °C under vacuum prior to use. The LFP counter electrodes were made by mixing partially delithiated LFP with Super P (TIMCAL) and PTFE in the ratio 8:1:1 (m/m/m). The electrodes were vacuum dried at 200 °C for 24 h. Before discharge cells were purged with high purity O₂ (N5.0).

Electrochemical Methods

Metal-O₂ cells with integrated pressure transducer were of the type PAT-Cell-Press (EL-Cell GmbH, Hamburg, Germany) with custom modified cathode plunger (see below). Electrochemical tests were run on a potentiostat/galvanostat (SP-300 or MPG-2, Bio-Logic).



Analytical Methods

High-performance liquid chromatography (HPLC) was used to determine the degree of the DMA to DMA-O₂ conversion as described earlier^[3]. The electrolyte was extracted from all cell components using 400 μ L DME, further sonicated in an ultrasonic bath for 10 min under exclusion of light and heat, centrifuged and the supernatant was transferred and DME removed by evaporation with N₂ stream at room temperature. The residue was dissolved in 500 μ L DME and a volume of 2 μ L was injected into the HPLC.

The yield of Li₂O₂ and of carbonaceous side products was determined using a previously described method that combines mass spectrometry and UV-Vis spectrometry.^[4] The washed electrodes were dried under vacuum and then subjected to the analysis. In short, as a first step the sample is acidified with 1 M H₂SO₄, upon which CO₂ evolves from Li₂CO₃. To quantify the dissolved peroxide, after CO₂ and O₂ evolution have ceased, part of the solution is removed and mixed with 2 wt% solution of Ti(IV)-oxysulfate solution in 1 M H₂SO₄ and analysed by UV-Vis on a Varian Cary 50 spectrometer. The remaining solution in the MS setup is then diluted with H₂O and Fenton's reaction to decompose organics into CO₂ is then initiated by adding FeSO₄ in 0.1 M H₂SO₄ and then H₂O₂ in 0.1 M H₂SO₄ under vigorous stirring.

¹O₂ was generated photochemically by illuminating O₂ saturated solutions containing 1 μ M of the photosensitizer Pd₄F at a wavelength of 643 nm. Photosensitization transfers energy from absorbed light to triplet oxygen. The process is initiated by the excitation of the photosensitizer from its S₀ ground state to its excited singlet state S_n, which then relaxes to the lowest excited singlet state S₁ and yields the triplet state T₁ via intersystem crossing (ISC). T₁ then transfers the energy to ³O₂ to form ¹O₂.

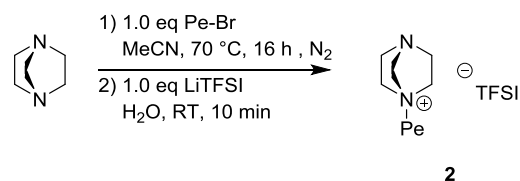
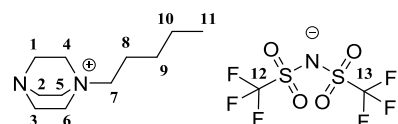
For measuring the quenching efficiency, a hermetically sealed quartz cuvette with a 1 mL head space, equipped with a stirring bar, was filled with 1 mL of a TEGDME solution containing Pd₄F and DMA in an Ar glovebox. The solution was bubbled with high purity oxygen at a flow rate of 1 mL·min⁻¹ for 20 min as well as during illumination. The cuvette was then placed in the UV-Vis spectrometer with a temperature controlled sample holder (22 °C). Prior to photooxygenation, a spectrum of the sample was recorded between 200 nm and 800 nm, to calculate the initial DMA concentration C_{DMA,0} according to Beer-Lambert's law $A = \varepsilon \cdot C \cdot d$ using the absorbance A at 379 nm. ε and d are extinction coefficient and light path length, respectively. Photooxygenation was performed by illuminating at a light density of 6.245 μ mol·s⁻¹·m⁻² for a given time, followed by 60 s stirring without illumination to ensure a homogeneous solution. After each photooxidation step, an absorbance spectrum was recorded. In consideration of the photo-sensitizer self-absorbance, all recorded spectra were subject to solvent background correction and baseline correction. Photo-bleaching and reactions with singlet oxygen of the photosensitizer were not observed, as the absorbance values of the Q- and Soret-band of the photosensitizer Pd₄F stayed constant over the time of the experiment. The decay of the DMA concentration was fitted to $C = C_0 \cdot \exp(-kt)$ to obtain the slope of DMA decay. The derivative $-C_0 \cdot k$ was used to compare the efficiency of the quenchers. This allows determining the relative rate of ¹O₂ reacting with DMA or being quenched by dividing the DMA consumption rate with quencher by the rate without quencher. NMR spectra were either recorded on a Bruker Avance III 300 MHz FT NMR spectrometer with autosampler (300.36 MHz (¹H-NMR), 75.53 MHz (¹³C-NMR)) or on a Varian Inova 500 MHz spectrometer (470.39 MHz (¹⁹F-NMR), 132.22 MHz (²³Na-NMR)). Chemical shifts δ are referenced to the residual protonated solvent signals as internal standard. ¹³C spectra were proton decoupled. Signal multiplicities J are abbreviated as s (singlet), d (doublet), t (triplet), and m (multiplet). For the correct assignment of the signals HH-COSY, HMBC and HSQC experiments were recorded if necessary. Moreover, the deuterated solvent, the chemical shifts δ in ppm, the coupling constant J in Hz and the integral and assignment of the respective signals are given. The deuterated solvent used was CDCl₃.

To assess the stability against Li₂O₂ and KO₂, 1 mg quencher was dissolved in 1 mL DME. For measuring stability against superoxide, 1.0 mg KO₂ were added to the quencher/DME solution in Ar atmosphere and stirred for 24 h. For measuring stability against peroxide, 1 mg Li₂O₂ were added to the quencher/DME solution in Ar atmosphere and stirred for 24 h. Solutions were then filtered, dissolved in CDCl₃ and subjected to ¹H-NMR spectrometry. To assess the stability against ¹O₂, 1 mg quencher were dissolved in 1 mL DME containing 1 μ M Pd₄F. The mixture was saturated with a stream of pure O₂ via a septum and the stirred solution irradiated with a red LED (643 nm) for 3 h in the closed vial with pure O₂ headspace.

Differential Scanning Calorimetry (DSC) measurements were done using a Perkin Elmer DCS 8500 instrument with a nitrogen purge gas flow of 20 mL/min and a heating/cooling rate of 10 °C/min.

Synthesis

1-pentyl-1,4-diazabicyclo[2.2.2]octan-1-ium bis(trifluoromethane)sulfon-imide (2)

**Figure S1.** Overview of the synthesis route for PeDTFSI (2, 1-pentyl-1,4-diazabicyclo[2.2.2]octan-1-ium bis(trifluoromethane)sulfon-imide).**Figure S2.** Structure of PeDTFSI.

An oven dried 100 mL round-bottom flask equipped with a Teflon[®]-coated magnetic stirring bar was charged with 1.00 g (8.92 mmol, 2.0 eq) diazabicyclo[2.2.2]octane and 10 mL MeCN. The colorless solution was stirred for 5 min at RT. Afterwards, 552 μ L (4.37 mmol, 1.0 eq) 1-bromopentane were added. The mixture was stirred for 16 h at 70 °C and the reaction controlled by ¹H-NMR spectroscopy. Afterwards, the reaction mixture was diluted with 30 mL Et₂O. Two Phases were formed and the denser layer was washed with Et₂O (3 \times 5 mL). The crude product was dried under vacuum at 10⁻² mbar for 5 h, then dissolved in 5 mL H₂O and 6.66 mL of a 0.5 M (3.33 mmol, 0.8 eq) lithium bis(trifluoromethane)sulfonimide solution in H₂O were added at room temperature. The mixture was stirred for 5 min and transferred into a separatory funnel. The aqueous phase was extracted with DCM (3 \times 20 mL). Subsequently the organic phase was washed with H₂O (3 \times 10 mL). The solvent of the organic phases was removed and to the residue 40 mL acetone and activated charcoal were added. The suspension was stirred for 3 h and filtered through a small plug of activated alumina. Finally, the solvent was removed and the product was dried in oil pump vacuum at 10⁻² mbar for 3 h. NMR and DSC analysis are given in Fig. S3.

Yield: 1.83 g (2.97 mmol, 68 % o. th.), colorless oil

C₁₃H₂₃F₆N₃O₄S₂ [463.45 g/mol]

mp: 43-49 °C

¹H-NMR (300.36 MHz, CDCl₃): δ = 3.32 (t, 6H, ³J_{HH} = 6.6 Hz, H-4, H-5, H-6), 3.13-3.27 (m, 8H, ³J_{HH} = 6.6 Hz, H-1, H-2, H-3, H-7), 1.61-1.79 (m, 2H, H-8), 1.26-1.44 (m, 4H, H-9, H-10), 0.91 (t, 3H, ³J_{HH} = 6.8 Hz, H-11).

¹³C{¹H}-NMR (75.53 MHz, CDCl₃): δ = 120.0 (J_{CF} = 322.0 Hz, C-12, C-13), 65.3 (J_{CN} = 2.4 Hz, C-7), 52.8 (J_{CN} = 3.1 Hz, C-4, C-5, C-6), 45.3 (C-1, C-2, C-3), 28.3 (C-10), 22.2 (C-9), 21.6 (C-8), 13.8 (C-11).

¹⁹F-NMR (470.39 MHz, DMSO-d₆): δ = -78.9.

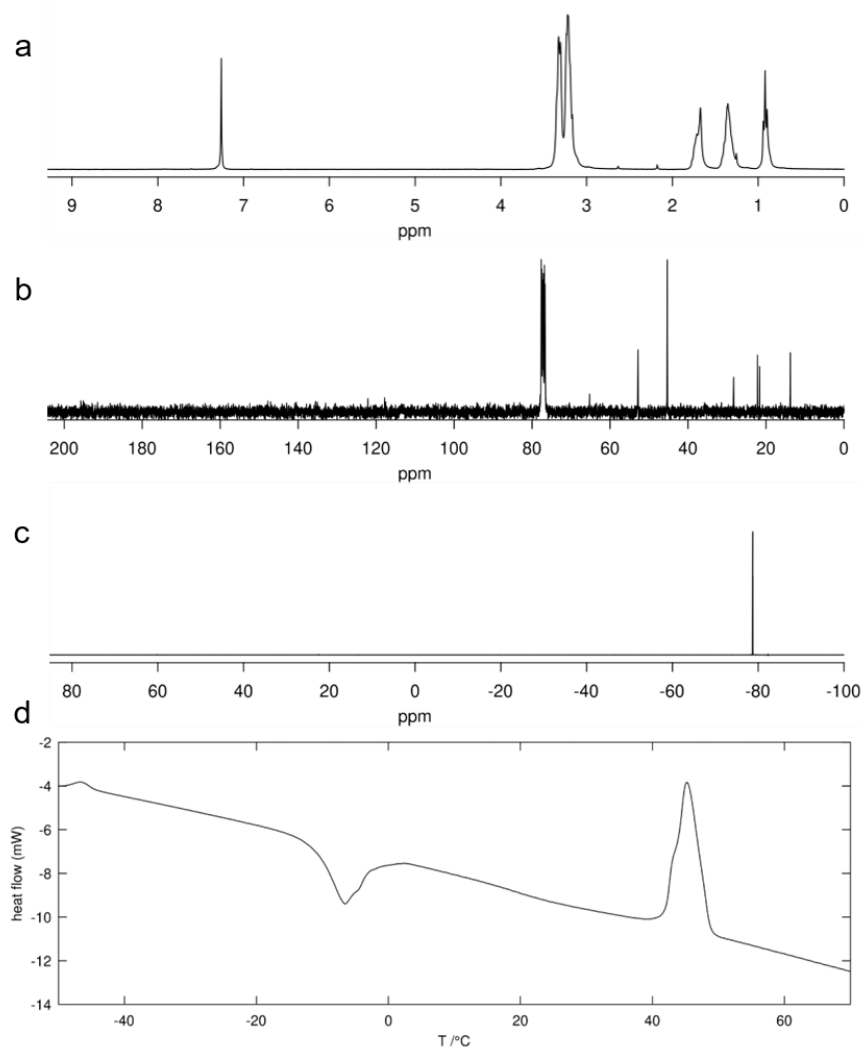


Figure S3. Characterisation of the PeDTFSI. a) ^1H -NMR; b) ^{13}C -NMR; c) ^{19}F -NMR; d) DSC analysis, 3rd heating phase (endothermal up).

Results and Discussion

Estimation of the donor number

The donor number (DN) of PeDTFSI was determined according to procedure by Johnson et al.²³ Na-shifts of 10 mM NaFSI dissolved in solvents with known DN were recorded to create a trend line (Table S1, Fig. S4) from which the DN of PeDTFSI could be estimated. For calibration a capillary filled with 1 M NaCl in D_2O was used.

Main Text Paragraph.

Table S1. Donor number and ^{23}Na -shifts of known solvent and PeDTFSI.

	DN	^{23}Na -shift (ppm)
MeCN	14	-6.43
DME	20	-5.83
NMP	27	-2.67
DMSO	30	-0.14
1,2-diaminoethane	55	12.96
TEGDME	12	-9.13
PeDTFSI	12.5	-8.81

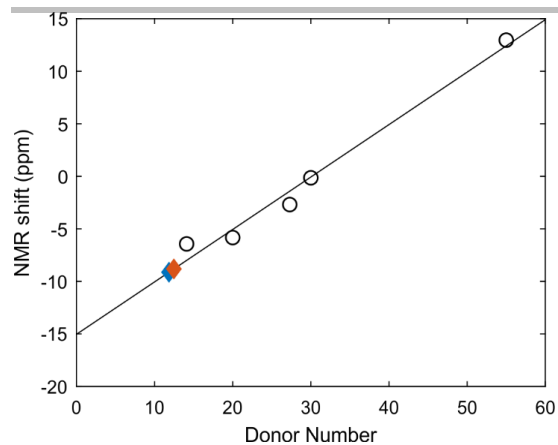


Figure S4. Determination of the donor number of PeDTFSI (orange) from a linear fit of ^{23}Na NMR shifts versus the known DNs of the solvents given in Table S1. TEGDME is shown in blue.

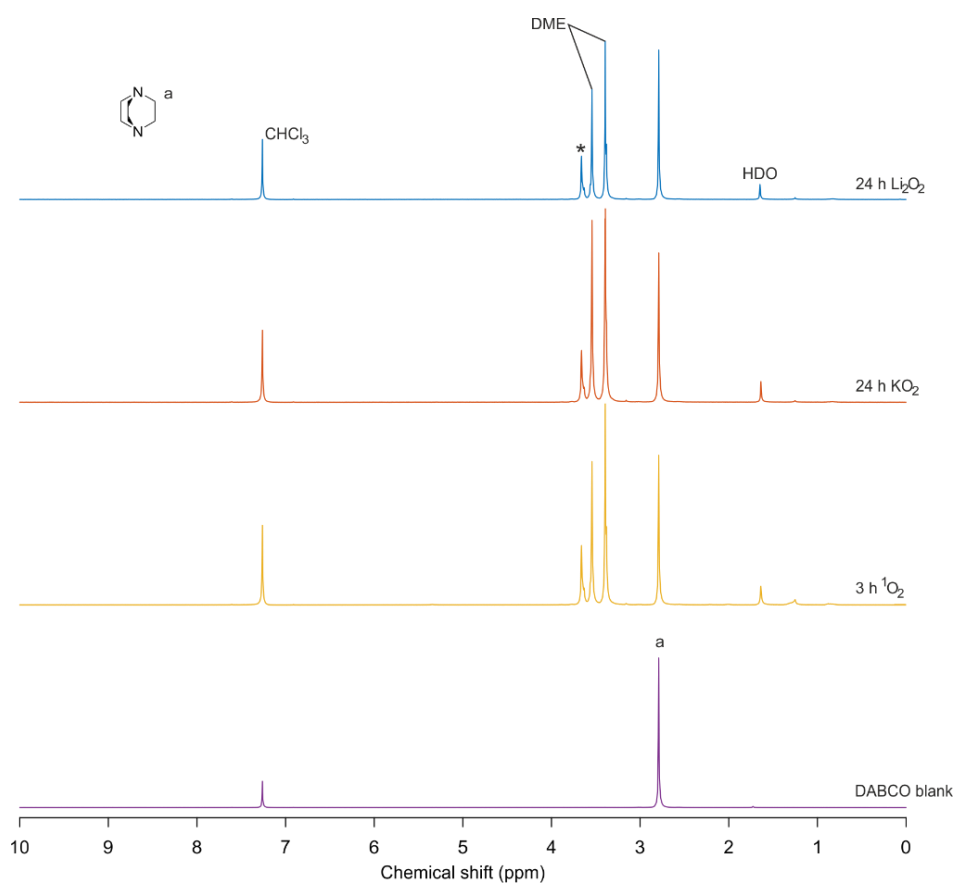


Figure S5. Stability of DABCO in contact with Li_2O_2 , KO_2 , and $^1\text{O}_2$. ^1H -NMR spectra (in CDCl_3) were recorded before and after 24 h contact with Li_2O_2 or KO_2 or 3 h in contact with $^1\text{O}_2$. The DMSO peak is taken as internal reference for quantitative comparison of spectra. The * denotes a residue from DME evaporation, which amounts to a content of ~ 1 ppm in the DME.

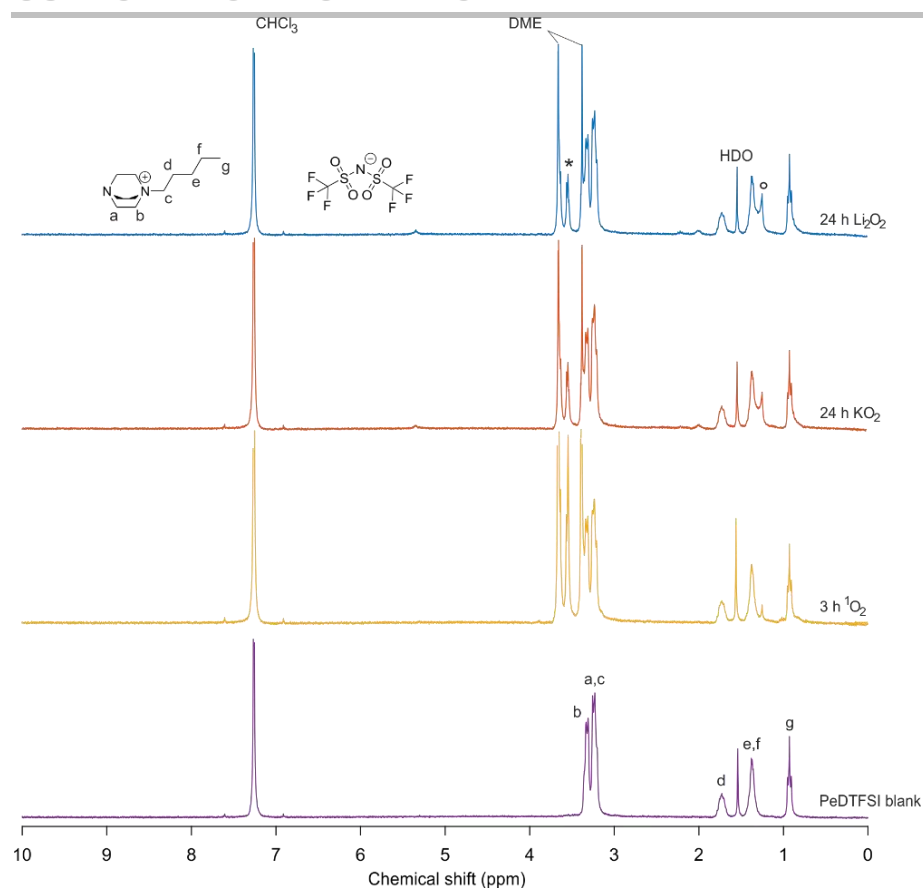


Figure S6. Stability of PeDTFSI in contact with Li_2O_2 , KO_2 , and $^1\text{O}_2$. $^1\text{H-NMR}$ spectra (in CDCl_3) were recorded before and after 24 h contact with Li_2O_2 or KO_2 or 3 h in contact with $^1\text{O}_2$. The DMSO peak is taken as internal reference for quantitative comparison of spectra. The * denotes a residue from DME evaporation, which amounts to a content of ~ 1 ppm in the DME; the ° denotes H from grease.

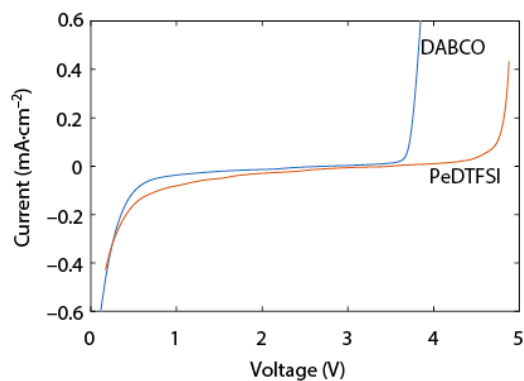


Figure S7. Linear sweep voltammetry of DABCO and PeDTFSI at a glassy carbon disc electrode in $0.1 \text{ M LiTFSI/TEGDME}$ containing 2 mM of the quencher. The scan rate was $50 \text{ mV}\cdot\text{s}^{-1}$.

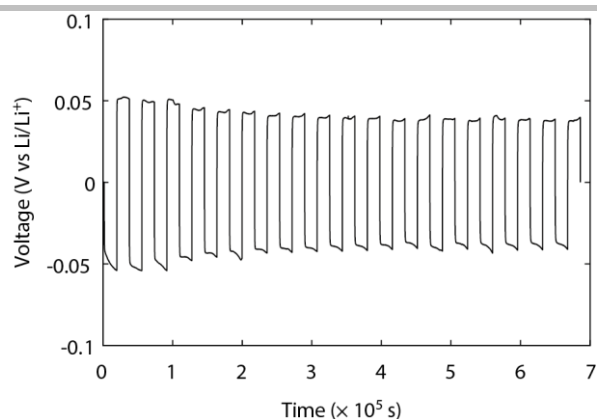


Figure S8. Cycling of a Li metal – Li metal cell in 1 M LiTFSI/TEGDME with 380 mM PeDTFSI at a current of 131 μA for 5 hours plating/deplating.

Impact of the quenchers on the $^1\text{O}_2$ generation rate

We determined the $^1\text{O}_2$ quenching efficiency of the quenchers by monitoring the disappearance rate of the $^1\text{O}_2$ trap DMA in presence of the quenchers during continuous photochemical $^1\text{O}_2$ generation as frequently used in the literature.^[6] $^1\text{O}_2$ is produced photochemically by illuminating O_2 -saturated solutions containing 1 μM of the photosensitizer palladium(II) *meso*-tetra(4-fluorophenyl)-tetrabenzoporphyrin (Pd₄F) at a wavelength of 643 nm.^[1] Photosensitization transfers energy from absorbed light to triplet oxygen^[6]. The process is initiated by the excitation of the photosensitizer from its S_0 ground state to its excited singlet state S_n , which then relaxes to the lowest excited singlet state S_1 and yields the triplet state T_1 via intersystem crossing (ISC). T_1 then transfers the energy to $^3\text{O}_2$ to form $^1\text{O}_2$.

The quencher may also quench the sensitizer T_1 state and hence reduce the $^1\text{O}_2$ generation rate. To determine this effect, we use the Stern-Volmer constant described in equation S1.

$$\tau_0/\tau = 1 + K_{\text{SV}} \cdot C_{\text{Q}} \quad (\text{S1})$$

Where C_{Q} is the quencher concentration, τ_0 is the fluorescence lifetime without quencher, τ the fluorescence lifetime at C_{Q} , K_{SV} is the Stern-Volmer constant. K_{SV} is represented by the product of the quencher rate coefficient k_{Q} and the lifetime τ_0 of the emissive excited state without a quencher.

We measured the lifetime of the T_1 state using the time domain measurement with help of a pulsed LED (Spectra LED, λ_{max} 392 nm) in combination with a DeltaHub module and Fluorolog 3 Spectrometer (all from Horiba Scientific). To eliminate potential interference by oxygen, the solution containing the sensitizer and a quencher in a screw-capped cuvette (Hellma) was purged with high purity nitrogen (99,9999%, Linde gas, Austria) for at least 15 min. The emission of the sensitizer was detected at 780 nm. The decay profiles are exemplified in Fig. S8 and are mono-exponential as expected. The Stern-Volmer plot in Fig. S9 shows that DABCO very inefficiently quenches the T_1 ($K_{\text{SV}} = 1.44 \text{ M}^{-1}$). K_{SV} is determined from the slope of the Stern-Volmer plot. This value is several orders of magnitude lower than the K_{SV} value for phosphorescence quenching by molecular oxygen. We were not able to detect any quenching by PeDTFSI up to 500 mM (Fig. S9).

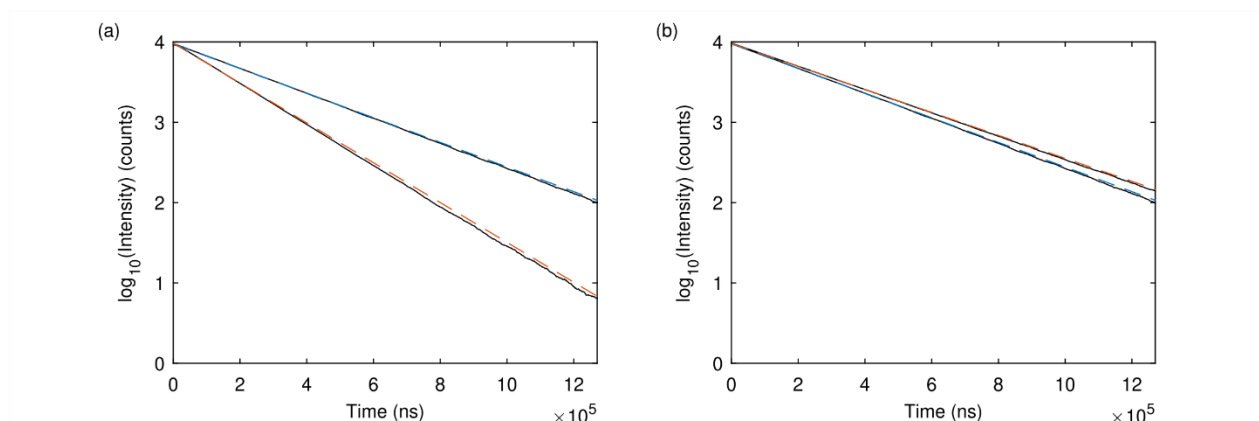


Figure S9. Influence of quenchers on the lifetime of the excited sensitizer T_1 state as seen by the decay of the emission at 780 nm for DABCO (a) and PeDTFSI (b). The orange curve represented the decay with quencher and the blue without. The dashed line is the exponential fit of the intensity and the full line the experimental data.

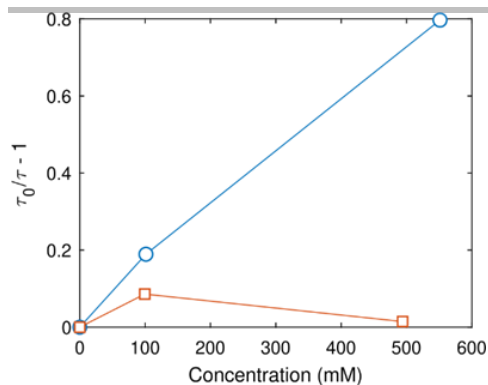


Figure S10. Stern-Volmer plots for potential phosphorescence quenching of the sensitizer. Very little quenching is seen for DABCO whereas no significant quenching is detected for PeDTFSI.

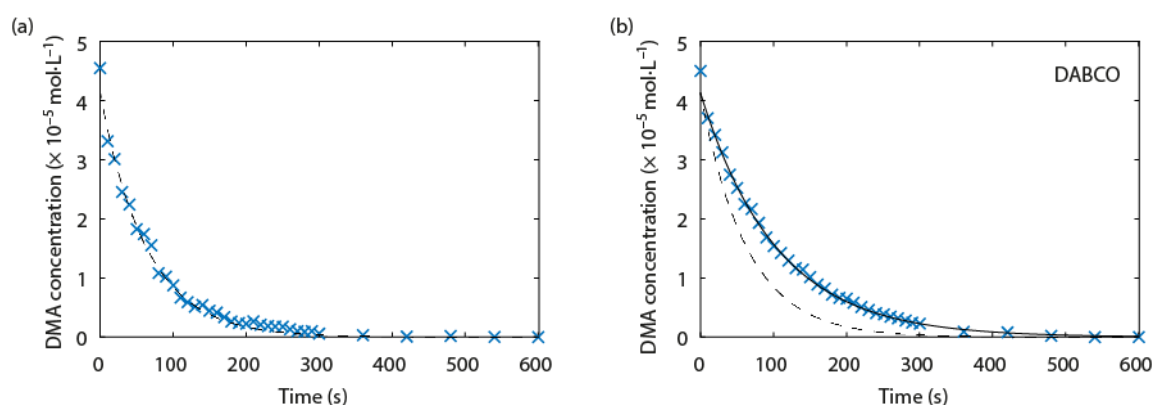


Figure S11. 9,10-dimethylanthracene (DMA) concentration versus time during 1O_2 generation in the presence of either no quencher (a) or DABCO (b) to determine quenching efficiency. $\sim 40 \mu\text{M}$ DMA and quencher in O_2 saturated TEGDME containing $1 \mu\text{M}$ Pd₄F were illuminated at 643 nm and the DMA concentration measured via the absorbance at 379 nm. The dashed line is the exponential fit of DMA consumption without a quencher, the full line is the exponential fit with the quencher.

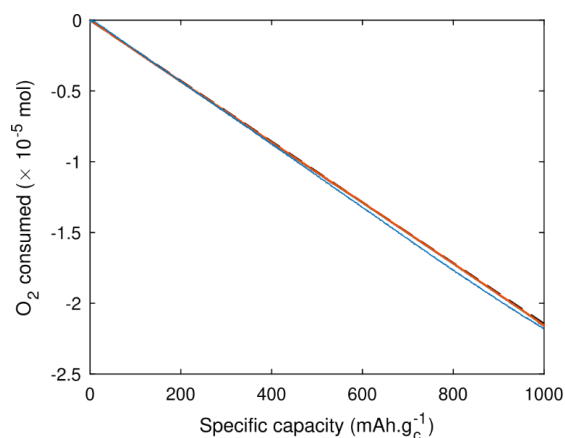


Figure S12. O_2 consumption vs. capacity upon discharge of carbon black/PTFE electrodes at a rate of $100 \text{ mA}\cdot\text{g}^{-1}$ in O_2 saturated TEGDME electrolytes that contained 1 M LiTFSI and either no additive (bue) or 0.38 M PeDTFSI (orange). The dashed line corresponds to the ideal rate of $2 e^-/O_2$.

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Y.K.P. Data curation: Lead; Methodology: Supporting; Visualization: Lead; Writing original draft: Supporting

C.L. Data curation: Equal; Visualization: Supporting

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E.M. Data curation: Supporting

L.S. Data curation: Supporting

C.S. Supervision: Supporting

S.M.B. Conceptualization: Equal; Data curation: Supporting; Methodology: Supporting; Formal analysis: Supporting; Resources: Supporting; Software: Supporting; Validation: Supporting; Writing – review & editing: Supporting

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