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Supporting Information

Visible light photooxidation of nitrate: The dawn of a nocturnal radical

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General Information

NMR Spectroscopy: NMR spectroscopy was carried out on either a Bruker Avance 400 (¹H: 400.13 MHz, ¹³C: 101 MHz, T = 300 K) or a Bruker Avance 300 (¹H: 300.13 MHz, ¹³C: 75 MHz, T = 295 K). The solvent residual peak (δ (CDCl₃): H 7.26; C 77.0) was used as an internal reference, chemical shifts were reported in δ [ppm], resonance multiplicities as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants *J* in Hertz [Hz]. The spectrometer is given for each spectrum.

Thin Layer Chromatography (TLC): For monitoring the reactions pre-coated TLC-sheets ALUGRAM Xtra SIL G/UV254 from Macherey-Nagel were used. The visualization was done by UV light (254nm or 366 nm) or staining with $CeSO_4/H_3Mo_{12}O_{40}P$.

Flash Column Chromatography: Standard flash chromatography was performed on an IsoleraTM Spektra Systems automated with high performance flash purification system using silica gel of particle size 40–63 μ m. Macherey-Nagel silica gel 60 M (230-440 mesh) was used for column chromatography.

Photochemical set-up, LEDs: Photocatalytic reactions were performed with 455 nm LEDs (OSRAM Oslon SSL 80 royal-blue LEDs, $\lambda_{em} = 455$ nm (± 15 nm), 3.5 V, 700 mA). Reaction vials (5 mL crimp cap vials) were illuminated from the bottom with LEDs and cooled from the side using custom made aluminum cooling block connected to a thermostat.



Figure S1 Photochemical set-up.

CV- Measurement

CV measurement was performed with the three-electrode potentiostat galvanostat PGSTAT302N from Metrohm Autolab using a glassy carbon working electrode, a platinum counter electrode and a silver wire as a reference electrode. The potential was achieved relative to the Fc/Fc+ redox couple (set by external reference). The control of the measurement instrument, the acquisition and processing of the cyclic voltammetric data were performed with the software Metrohm Autolab NOVA 1.6.013. The measurements were carried out as follows: a 0.1 M solution of TBATFB in MeCN was placed in the measuring cell and the solution was degassed by a stream of argon for 5 min. After measuring of the baseline LiNO₃ was added (1 mL, 0.01 M in MeCN) and the solution was degassed by Argon purge for 5 min. The cyclic voltammogram was recorded with a single scan using Fc/Fc⁺ as internal standard with a scan rate of 50 mV/s. The potentials were converted to SCE according to V. V. Pavlishchuk and A. W. Addison.^[1]



Figure S2 Cyclovoltammogram of LiNO₃ in MeCN at 25°C.

UV/VIS and emission spectroscopy

The UV-Vis measurements with online irradiation were performed on a self-made apparatus using a fluorescence cuvette in a fluorescence cuvette holder, LED (Cree-XP, royal blue, 455 nm) placed perpendicular to the optical pathway of the Agilent 8453 UV-Vis Spectrometer (Figures S3 and S4). The measurement was performed in 10 mm Hellma fluorescence quartz cuvettes

(117.100F-QS) with a screw cap with PTFE-coated silicon septum. To obtain differential spectra the measured solution in darkness without LED irradiation was used as blank reference.



Figure S3 Setup for UV-Vis measurement with online irradiation.



Figure S4 Scheme of the setup for UV-Vis measurement with online irradiation.

The measurement was performed with a solution of 9-mesityl-10-methylacridinium perchlorate (1) ($c=5\mu$ M) and LiNO₃ ($c=0,5*10^{-3}$ M) in MeCN under argon atmosphere. The spetra were taken online during irradiation. The aerated spectrum was taken after opening the cuvette and shaking the sample under continuous irradiation. The ground state absorption of the catalyst cannot be fully recovered due to photobleaching of the catalyst.



Figure S5 Spectra of the reduced catalyst Acr'-Mes formed upon irradiation in the presence of $LiNO_3$ under inert atmosphere after 120 s (green) and 240 s (blue). The purple curve shows the catalyst after 240 s of irradiation without $LiNO_3$. The orange curve shows the irradiated sample after exposure to air.

Fluorescence quenching

Fluorescence measurements were performed with Horiba FluoroMax-4 fluorimeter, 10 mm Hellma fluorescence quartz cuvettes (117.100F-QS) with a screw cap with PTFE-coated silicon septum was used. The quenching experiment was performed with a 5 μ M solution of Acr⁺-Mes in MeCN in open air with 50 eq. LiNO₃ (excitation wavelength: 420 nm).



Figure S6 (a) Formation of the reduced catalyst **Acr'-Mes** in the presence of LiNO₃ under anaerobic conditions after 120 s and 240 s of continuous irradiation. (b) Quenching of the fluorescence of excited **Acr⁺-Mes** by LiNO₃ indicating a reaction from the singlet state.

UV/VIS

UV–Vis analyses were performed with Varian Cary 50 UV/Vis spectrophotometer and Agilent 8453 UV-Vis Spectrometer. To observe the photostability of the catalyst **1** (Mes^+Acr) during the reaction we measured a UV/VIS spectrum of the reaction mixture before the irradiation and after 1h of irradiation. The reaction mixture contained *tert*-butylcyclohexanol (0.25 mmol), **1** (5 mol%) and LiNO₃ (0.5 mmol, 2 eq.) in 1 mL MeCN in open air, for UV/VIS measurements the solution was diluted 1:10 with pure MeCN. Figure S6 shows a strong photobleach of the catalyst **1** after 1 h of irradiation. This degradation of **1** is likely due to oxidation of the mesityl-moiety by NO₃[•].



Figure S7 Absorption spectra of the reaction mixture before irradiation (blue curve) and after 1h of irradiation with 455 nm (red curve).

Laser flash photolysis

Material. Burdick and Jackson HPLC grade acetonitrile and Aldrich tetrabutylammonium nitrate were sourced commercially and used as received. 9-Mesityl-10-methylacridinium Perchlorate was purchased from TCI chemicals and was recrystallized from MeOH/MeCN and ether prior to use.^[2]

Laser Flash Photolysis studies were conducted on an Edinburgh Instruments LP920 spectrometer using the third harmonic of a Quantel Brilliant B Nd:YAG LASER (6 ns pulse, 355 nm) as the excitation source. All experiments were performed with the laser operating at a nominal power rating of 20-30 mJ per pulse. The detection system employs a Hammamatsu R2856 photomultiplier tube interfaced with a Tektroniz TDS 3012C Digital Phosphor oscilloscope for transient absorption spectra; wavelength resolved spectra were collected using an ANDOR DH720 ICCD camera. Measurements of the photochemical reactions of Acr⁺-Mes with NO₃ were performed according to the following procedure. MeCN solutions of Acr⁺-Mes ClO₄ (1 x 10⁻⁴ M) were sparged with nitrogen alone or in the presence of Bu₄N NO₃ (1 x 10⁻³ M). Each individual transient and spectra represents 15-100 averages.



Figure S8 Laser flash photolysis of Mes⁺-Acr and LiNO₃ under N₂-atmosphere.

As depicted in Figure S7 LFP measurements showed that no quenching of the observed excited triplet state (CT^{T} or LE^{T}) by NO_{3}^{-} occurs. This supports a reaction from a short-lived singlet

excited state as proposed in the mechanism. The singlet excited state has already decayed after 30 ns and thus cannot be observed. Figure S8 shows that in the measurements after 10 ns and 20 ns some contribution from the fluorescence of the singlet state can still be detected. The calculated differential spectra of the measurement after 10 ns and 30 ns match with the reported fluorescence spectra.



Figure S9 Measurements after 10 ns and 20 ns still show some contributions from the singlet state emission.

General procedure A: Photocatalytic oxidation of diphenylacetylene (2)

In a 5 mL crimp cap vial 45 mg (0.25 mmol, 1 eq.) diphenylacetylene (2), the respective amount of LiNO3, and 5 mg (5 mol%) 9-mesityl-10-methylacridinium perchlorate (1) were dissolved in 1 mL MeCN, equipped with stirring bar and irradiated for 2 h with high power LEDs (λ = 455 nm) in open air. The temperature was kept constant at 22 °C. After the irradiation period 0.1 mmol of the GC-standard acetophenone (100 µL of a 1.0 M stock solution) was added to the reaction mixture. The mixture was filtered and submitted to GC analysis without further work-up.



Figure S10 Example of the GC spectra obtained from the oxidation of compound 2.

GC was calibrated using a three-point calibration; the calibration curve for benzil is shown as an example. The GC oven temperature program was adjusted as follows: initial temperature 40°C was kept for 3 minutes, the temperature was increased at a rate of 15°C/min over a period of 16 minutes until the final temperature (280°C) was reached and kept for 5 minutes



Figure S11 Exemplary calibration curve for benzil 3.

Synthesis of starting material compound 9

Synthesis of compound 9 was performed according to literature known procedures.^[3]

(1R,2S)-2-(Hex-1-yn-1-yl)cyclohexan-1-ol (12)



¹**H NMR** (400 MHz, CDCl₃) δ 3.40 – 3.31 (m, 1H), 2.33 (s, 1H), 2.20 – 2.12 (m, 3H), 2.02 – 1.89 (m, 1H), 1.77 – 1.09 (m, 11H), 0.90 (t, J = 7.2 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 82.8, 81.0, 73.9, 39.2, 32.9, 31.4, 31.1, 25.0, 24.3, 21.9, 18.4,

C NMR (101 MHZ, CDC13) 0 82.8, 81.0, 73.9, 39.2, 32.9, 31.4, 31.1, 25.0, 24.3, 21.9, 18.4, 13.6.

(1R,2S)-1-Ethoxy-2-(hex-1-yn-1-yl)cyclohexane (9)



¹**H** NMR (400 MHz, CDCl₃) δ 3.54 – 3.42 (m, 2H), 3.14 (td, *J* = 8.1, 3.9 Hz, 1H), 2.41 – 2.30 (m, 1H), 2.14 (tdd, *J* = 6.9, 2.2, 1.1 Hz, 2H), 1.99 – 1.83 (m, 2H), 1.69 – 1.15 (m, 12H), 0.90 (dt, *J* = 12.7, 7.3 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 82.4 (C_q), 81.1 (C_q), 80.1(-CH-), 71.1 (-O-*CH*₂-), 35.1(-CH-), 31.2 (-CH₂-), 30.7 (-CH₂-), 30.2 (-CH₂-), 24.0 (-CH₂-), 23.3 (-CH₂-), 21.9 (-CH₂-), 18.5(-CH₂-), 13.6 (-CH₃), 11.6 (-CH₃).

(1S,2R)-1-(Hex-1-yn-1-yl)-2-propoxycyclohexane



¹³C NMR (75 MHz, CDCl₃) δ 82.3 (C_q), 81.17(C_q), 80.2 (-CH-), 71.1 (-O-*CH*₂-), 35.2 (-CH-), 31.2 (-CH₂-), 30.8 (-CH₂-), 30.3 (-CH₂-), 24.1 (-CH₂-), 23.4 (-CH₂-), 23.1 (-CH₂-), (-CH₂-), 18.5 (-CH₂-), 13.7(-CH₃), 10.7 (-CH₃).

Photooxidation of compound 9

Two vials each with 52 mg (0.25 mmol, 1 eq.) of the alkyne ether **9** and 35 mg LiNO₃ (2 eq., 0.5 mmol) suspended in 0.5 mL of MeCN were irradiated with LEDs (λ =455 nm). To this mixture a solution of 5 mg (5 mol%) catalyst **1** was added via a syringe pump (rate: 0.5 mL/h).

The total irradiation time was 6 h. After irradiation the two reaction mixtures were combined, diluted with water and extracted three times with diethyl ether. The combined organic layers were dried over Na_2SO_4 , filtered and concentrated in vacuum. The resulting crude product was further purified by column chromatography using diethyl ether in pentane (2:10) as an eluent.



Yield: 21% (0.11 mmol)

NMR data is in accordance with literature.^[4]

¹**H** NMR (300 MHz, CDCl₃) δ 4.36 (dq, J = 9.6, 6.4 Hz, 1H), 3.09 (td, J = 10.4, 3.8 Hz, 1H), 2.94 (dd, J = 11.1, 9.6 Hz, 1H), 2.34 (t, J = 7.4 Hz, 2H), 2.05 (dt, J = 7.0, 3.0 Hz, 1H), 1.80 (ddd, J = 12.2, 8.7, 3.1 Hz, 3H), 1.64 (dt, J = 19.1, 7.8 Hz, 2H), 1.57 – 1.42 (m, 2H), 1.41 – 1.08 (m, 7H), 0.98 (d, J = 6.4 Hz, 3H), 0.85 (t, J = 7.3 Hz, 3H).

Yield: 37% (0.19 mmol)

NMR data is in accordance with literature.^[4]

¹**H** NMR (400 MHz, CDCl₃) δ 4.12 (td, J = 9.5, 3.8 Hz, 1H), 3.12 (td, J = 10.5, 3.8 Hz, 1H), 2.98 (dd, J = 10.9, 9.7 Hz, 1H), 2.39 (t, J = 7.4 Hz, 2H), 2.14 – 2.06 (m, 1H), 1.85 – 1.75 (m, 3H), 1.72 – 1.64 (m, 2H), 1.58 – 1.48 (m, 2H), 1.41 – 1.21 (m, 6H), 1.07 – 0.95 (m, 1H), 0.90 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 210.0 (C_{carbonyl}), 82.5 (-(CH₂)₂-*CH*-O), 80.0 (-(CH₂)₂-*CH*-O), 58.9 (-CH-), 47.3 (-CH-), 45.2 (-CH₂-), 31.4 (-CH₂-), 28.2 (-CH₂-), 26.2 (-CH₂-), 25.6 (-CH₂-), 25.5 (-CH₂-), 24.2 (-CH₂-), 22.3 (-CH₂), 13.9 (-CH₃), 10.8 (-CH₃).

Proposed mechanism for the photooxidation of compound 9

Scheme S1 shows the mechanism of the cyclization as proposed in previous reports.^[3, 5] In the first step a nitrate radical adds to the triple bond of alkyne-ether **9** which leads to a vinylic radical. Subsequent hydrogen abstraction of the H-atom in α -position of the ether leads to radical intermediate which cyclizes to product **10**. A crucial step which could account for lower yields is the non-regioselective first step, the addition of the nitrate radical to the alkyne **9**, if the opposite side of the triple bond is attacked, no product will be formed.



Scheme S1 Proposed mechanism for the self-terminating radical cyclization of 9 by NO₃.

General Procedure B: Nitrate mediated alcohol oxidation

In a 5 mL crimp cap vial 0.25 mmol (1 eq.) of the alcohol, 17 mg (0.25 mmol, 1 eq.) LiNO₃, and 5 mg (5 mol%) 9-mesityl-10-methylacridinium perchlorate (**1**) were dissolved in 1 mL MeCN, equipped with stirring bar and irradiated with high power LEDs (λ = 455 nm) in open air until complete bleaching of the yellow color of catalyst **1** (ca. 2-3 h depending on the substrate). Then another 5 mg (5 mol%) of **1** was added to the reaction mixture and irradiated to a total time of 6 h. The temperature was kept constant at 22°C. After the irradiation period the mixture was diluted with water and extracted three times with diethylether. The combined organic phases

were dried over Na_2SO_4 , filtered and concentrated in vacuum. The resulting crude product was further purified by column chromatography using petroleum ether/ ethyl acetate as the eluent (20-40 % ethyl acetate in petroleum ether).

4-(*tert*-Butyl)cyclohexan-1-one (14a)^[6]

¹**H NMR** (300 MHz, CDCl₃) δ 2.42 – 2.27 (m, 4H), 2.12 – 2.05 (m, 2H), 1.50 – 1.39 (m, 3H), 0.92 (s, 9H).

Isomenthon (14b)

¹**H** NMR (300 MHz, CDCl₃) δ 2.35 – 2.25 (m, 1H), 2.15 – 2.06 (m, 1H), 2.05 – 1.89 (m, 3H), 1.78-1.63 (m, 2H), 1.54 – 1.38 (m, 2H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.84 (d, *J* = 6.5 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 213.8, 56.2, 47.0, 33.4, 28.4, 26.8, 25.9, 20.5, 19.9, 18.9.

(1S,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one (Camphor) (14c)^[7]



¹**H NMR** (300 MHz, CDCl₃) δ 2.40 – 2.27 (m, 1H), 2.08 (t, J = 4.5 Hz, 1H), 2.02 – 1.87 (m, 1H), 1.84 (d, J = 18.2 Hz, 1H), 1.74 – 1.57 (m, 2H), 1.46 – 1.26 (m, 2H), 0.95 (s, 3H), 0.90 (s, 3H), 0.83 (s, 3H).

4-Nitrobenzaldehyde (14d)^[8]

Ĥ O_2N

¹**H NMR** (300 MHz, CDCl₃) δ 10.16 (s, 1H), 8.40 (d, J = 8.7 Hz, 2H), 8.08 (d, J = 8.8 Hz, 2H).

Methyl 2-oxo-2-phenylacetate (14f)^[9]

O COOMe

¹**H NMR** (300 MHz, CDCl₃) δ 8.05 – 7.99 (m, 2H), 7.67 (m, 1H), 7.56 – 7.47 (m, 2H), 3.98 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 186.1, 164.1, 135.0, 132.4, 130.1, 128.9, 52.8.

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