Electronic Supplementary Information

Direct photochemical activation of non-heme Fe(IV)=O complexes

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Experimental Details

Synthesis. The ligand 1,1-di(pyridin-2-yl)-N,N-bis(pyridin-2-ylmethyl)methanamine (N4Py),¹ 1,1-di(pyridin-2-yl)-N,N-bis(pyridin-2-ylmethyl)ethan-1-amine (MeN4Py),² $[(N4Py)Fe^{II}(CH_3CN)](CIO_4)_2$ (1a),² $[(MeN4Py)Fe^{II}(CH_3CN)](CIO_4)_2$ (2a), and $[(Bn-TPEN)Fe^{II}(OTf)](OTf)$ (3a)³ were prepared as reported previously. Commercially available chemicals were purchased from Sigma Aldrich without further purification. All solvents used for spectroscopy were of UVASOL (Merck) grade.

[(N4Py)Fe^{IV}(O)](PF₆)₂ (1). Cerium ammonium nitrate (CAN) (208 mg, 0.38 mmol) in water (0.3 mL) was added to [(N4Py)Fe^{II}(Cl)](Cl) (85.3 mg, 0.17 mmol) in acetonitrile/water (1:1 v/v, 3.5 mL). A blue solid crashed out of the solution upon addition of aqueous KPF₆ (210 mg, 1.15 mmol in 2 mL water). The precipitate was recovered by vacuum filtration, washed with 4 mL water and dried in a desiccator for 3 h. The complex [(N4Py)Fe^{IV}(O)](PF₆)₂ (4)⁴ was obtained as blue solid in 68.5% yield (86 mg, 0.07 mmol). ¹H NMR (400 MHz, CD₃CN) δ (ppm) 44.12, 30.02, 9.70, 8.55, -10.49, -16.16, and -19.91.

[(MeN4Py)Fe^{IV}(O)](PF₆)₂.2H₂O (2). Cerium ammonium nitrate (CAN) (339 mg, 0.62 mmol) in water (0.6 mL) was added to [(MeN4Py)Fe^{II}(Cl)](Cl).2H₂O (160.8 mg, 0.28 mmol) in water (16 mL). A blue solid precipitated upon addition of aqueous KPF₆ (517 mg, 2.8 mmol in 4 mL water). The precipitate was recovered by vacuum filtration, washed with 4 mL of water and air-dried for 1 h. The complex [(MeN4Py)Fe^{IV}(O)](PF₆)₂.2H₂O (2) was obtained as blue solid with 71% yield (178 mg, 0.24 mmol). ¹H NMR (400 MHz, CD₃CN) δ (ppm) 44.4, 30.7, 9.86, 8.5, -9.4, -12.76, -15.61 and -18.8. Anal. calcd for $C_{24}H_{23}N_5FeOP_2F_{12}$: C 38.8, H 3.12, N 9.42; Found: C 38.2, H 3.12, N 9.19.

Physical methods.

UV-vis absorption spectra were recorded with a Specord600 (AnalytikJena) spectrophotometer in 1 cm (unless stated otherwise) path length quartz cuvettes. Unless stated otherwise all measurements were

performed at 21 °C. EPR (X-band, 9.46 GHz) were recorded on a Bruker ECS106 spectrometer in liquid nitrogen (77K). Samples (0.4 mL) was fast frozen in liquid nitrogen according to the UV-vis absorption spectra.

Photochemistry Typical experiments used 2 mL of solution of **1** - **3** (0.125 mM) in the 1 cm pathlength cuvette. The light source was orthogonal to the monitoring beam of the UV-vis absorption spectrometer. LEDs (Thorlabs) were used at 365 nm (M365 F1, 6.10×10^{-5} einstein s⁻¹ dm⁻³ or, for power dependent studies, M365LP1-C5, 1.19×10^{-5} einstein s⁻¹ dm⁻³, Figure S1 and S7)), 490 nm (M490F3, 4.76×10^{-6} einstein s⁻¹ dm⁻³), 565 nm (M565F, 3.19×10^{-6} einstein s⁻¹ dm⁻³), 660 nm (M660F1, 4.0×10^{-6} einstein s⁻¹ dm⁻³), and 300 nm (M300F2, 1.25×10^{-6} einstein s⁻¹ dm⁻³) controlled by T-Cube Light Source & Driver Module (Thorlabs); or a DPSS laser at 355 nm (9.79 $\times 10^{-6}$ einstein s⁻¹ dm⁻³, Cobolt Lasers). For all irradiations, the power at the sample was measured with PM10V1 High Power 10 Watt sensor coupled to a FieldMate Power Meter.

Estimation of photochemical quantum yield.

The overall photochemical quantum yield was calculated according to literature methods with modification for the photo-reduction process.^{5,6}

The photo reduction of **1** was calculated using equation 1:

$$-V\frac{dC_1}{dt} = \phi_1 \frac{\varepsilon_1 C_1}{A} I(1 - 10^{-A})$$
(E1)

 $-\frac{dC_1}{dt}$ is the rate of change of concentration of **1** in M, I(1 – 10^{-A}), the light absorbed by the whole sample, $\frac{\varepsilon_1 C_1}{A}$ is the fraction of the light absorbed by **1**, C₁ is the concentration of **1** in M, ε_1 is molar absorptivity of **1** at λ_{irr} , A is the absorbance when using a 1 cm path length cuvette, ϕ_1 is quantum yield for the photoreduction, I is radiant power (*Einsteins s⁻¹ L⁻¹*).

$$-\frac{dC_1}{dt} \cdot \frac{A}{1-10^{-A}} = \varepsilon_1 I \phi_1(C_1) \tag{E2}$$

With $K = \varepsilon_1 I \phi_1$,

$$-\frac{dC_1}{dt} \cdot \frac{A}{1 - 10^{-A}} = K(C_1)$$
(E3)

With $f = \int_0^t \frac{1 - 10^{-D}}{D} dt$, and integration;

$$\ln\frac{(KC_1)}{(KC_0)} = f K$$
(E4)

then,

$$\ln\frac{(c_1)}{(c_0)} = f K$$
(E5)

linear fitting of f and $\ln \frac{(C_1)}{(C_0)}$, gives the slope K,

$$\mathbf{K} = \varepsilon_1 I \phi_1, \qquad \phi_1 = \frac{\mathbf{K}}{\varepsilon_{1 \times I}} \tag{E6}$$

Quantification of formaldehyde formation

The formation of formaldehyde was quantified as described in the literature.⁷ The colourimetric reagent was prepared by dissolving NH₄OAc (15 g, 0.19 mol), acetic acid (0.3 mL, 5.4 mol) and pentane-2,4dione (0.2 mL, 1.9 mol) in 100 mL water. 0.5 mL of reaction solution was diluted (0.5 mL reaction solution and 0.5 mL H₂O), then mixed with another 1 mL of colourimetric reagent. The standard samples were prepared with known concentrations (0.125, 0.25, 0.5, 1.0, and 2 mM) of formaldehyde solution with the same procedure (0.5 mL formaldehyde solution, 0.5 mL H₂O and 1 mL colourimetric solution). The 6 samples were held at 31 °C in a temperature controlled 8-cell sample holder and monitored by UV-vis absorption spectroscopy, until the increase of the absorbance at 412 nm of diacetyldihydrolutidine ceased. The concentration of formaldehyde was calculated from the calibration curve obtained from known concentrations of formaldehyde.



Figure S 1. (left) Absorbance at 696 nm of **1** (0.125 mM) in acetonitrile in dark and under irradiation (λ_{exc} 365 nm) at 21 °C with light intensities of 340 mW (red squares), 260 mW (green circles), 150 mW (blue triangles), 50 mW (Cyan triangles), (left axis normalized absorbance, right axis actual absorbance). (right) Dependence of k_{obs} value on irradiation power obtained by linear fitting (green lines in left graphic) of the first 250 s of the decay.



Figure S 2. UV-vis absorption spectra of the photo product ($\lambda_{exc} = 365 \text{ nm}$) of **1** (0.125 mM, black) in acetonitrile with **1a** (0.125 mM, red) in acetonitrile.



Figure S 3. Absorbance at 454 nm (right y-axis) and at 696 nm (left y-axis) with 1 (0.125 mM) in acetonitrile over time during irradiation at 365 nm under aerobic (black) and anaerobic (red) conditions at 21 $^{\circ}$ C.



Figure S 4. Absorbance at 454 nm (red arrow, right y-axis) and at 696 nm (black arrow, left y-axis) with 1 in CH₃CN (black) over time with irradiation at 365 nm and CD₃CN (red), at 21 $^{\circ}$ C.



Figure S 5. (a) X-band EPR (77 K) spectra of **1** (0.5 mM) in acetonitrile under irradiation 365 nm; sample was flash frozen at ca. 30% (black, double integration (spins) = 2.332×10^8) and at 66% (red, double integration = 4.565×10^8) photo-reduction of **1** at 21 °C. Inset shows the corresponding UV-vis absorption spectra. (b) Expansion of the 2800 - 3500 G range, and comparison with a 0.5 mM solution of [(N4Py)Fe^{III}(OCH₃)]²⁺ (in blue, double integration = 8.262×10^8). Considering the formation of Fe^{II} (~ 0.1 mM, calculated from the absorbance at 454 nm ($\epsilon_{454 \text{ nm}}$ **1a** = 6520 M⁻¹ cm⁻¹)), it can be concluded that the loss of **1** (0.5 mM × 66% = 0.33 mM) was due to the formation of Fe^{III} (~ 0.27 mM) and Fe^{II} (~ 0.1 mM).



Figure S 6. UV-vis absorption spectrum of **2** (0.125 mM) in acetonitrile before (black) and during irradiation at 365 nm (dashed lines) with the final spectrum in red. Inset: absorbance at 686 nm (black, left y-axis) and 458 nm (red, right y-axis) over time at 21 °C. See Figure 4 for changes in absence of irradiation and with visible irradiation.



Figure S 7. Absorbance at 458 nm and at 686 nm with 2 (0.125 mM) with acetonitrile over time under irradiation at 300 nm at 21

°C.



Figure S 8. (left) change in absorbance at 740 nm of **3** (0.125 mM) in acetonitrile under irradiation (λ_{exc} 365 nm) at 21 °C at 50 mW (black squares), 150 mW (red circles), 260 mW (green triangles), 340 mW (blue triangles) at 21 °C. (right) Dependence of k_{obs} obtained by linear fitting of the first 250 s of the decay (green lines in left graphic) with irradiation power. See Figure 3 in main text for decay in absence of irradiation.



Irradiation of 1 in the presence of benzyl alcohol or ethylbenzene at 21 °C

Figure S 9. Absorbance at 696 nm of **1** (0.5 mM) and absorbance at 454 nm (showing an increase with time, right axes), in the presence of (left) 5 equiv. benzyl alcohol (**BA**) and (right) 50 equiv. ethylbenzene (**EB**), in CH₃CN at 21 °C with (red, $\lambda_{exc} = 365$ nm) and without irradiation (black). The changes in absorbance in the absence of substrate (**BA** and **EB**) are shown in blue. The slopes obtained from linear fitting of the first 500 s (green lines) are summarized in Table S1.

	substrates	Rate of decrease in absorbance of Fe ^{IV} =O $(\times 10^{-5} \text{ s}^{-1})^{a}$	Rate of increase in absorbance of $Fe^{II} (\times 10^{-4} s^{-1})^b$
Under irradiation	5 equiv. BA (C ₆ H ₅ CH ₂ OH)	23	10
	50 equiv. EB $(C_6H_5C_2H_5)$	16	5.2
	CH ₃ CN only	12	1.1
In Dark	5 equiv. BA (C ₆ H ₅ CH ₂ OH)	5.1	0.17
	50 equiv. EB $(C_6H_5C_2H_5)$	3.1	0.03
	CH ₃ CN only	<0.001	<0.001

Table S1. Comparison of the rate of the change of 1 under irradiation and in the dark at 21 °C with and without ethylbenzene or benzyl alcohol

Values are obtained by linear fitting the changes of the absorbance at 696 nm^a and 454 nm^b for the first 500 s of the reaction.



Irradiation of 1 in the presence of benzyl alcohol at -30 °C.

Figure S 10. Change in absorbance of 1 (0.5 mM) in acetonitrile at 696 nm over time in the presence of 5, 20 and 50 equiv. benzyl alcohol in the dark (left) and under irradiation at 365 nm (right) at -30 °C. Green lines show linear fitting over the first 500 s summarized in Table S2.

Table S2. Observed rate of change in absorbance of 1 under irradiation and dark in the presence of benzyl alcohol at -30 °C.

Substrate equiv. w.r.t 1	Under irradiation ($\times 10^{-4} \text{ s}^{-1}$)	In Dark ((× 10^{-6} s^{-1})
5 equiv.	1.0	2.7
20 equiv.	1.3	8.5
50 equiv.	1.5	20

Values are obtained by linear fitting the decrease of the absorbance at 696 nm^a for the first 500 s of the reaction.



Comparison of the reactivity of 1 with benzyl alcohol and cyclohexanol at -30 °C.

Figure S 11. Comparison of change in absorbance at 696 nm (left) and at 454 nm (right) with **1** (0.5 mM) in acetonitrile at -30 $^{\circ}$ C. In dark; with 50 equiv. (dark blue) cyclohexanol-H₁₂, (green) cyclohexanol-D₁₂; Under irradiation at 365 nm (cyan) in absence of cyclohexanol; and with 50 equiv. (black) cyclohexanol-H₁₂, and with 50 equiv. (red) cyclohexanol-D₁₂. Black lines indicate the linear fitting of the changes over the first 500 s, see Table S3 for data.



Figure S 12. Comparison of change in absorbance at 696 nm (left) and at 454 nm (right) with **1** (0.5 mM) in acetonitrile at -30 °C. In dark; with 50 equiv. (red) benzyl alcohol- α , α -H₂, (black) benzyl alcohol- α , α -D₂; Under irradiation at 365 nm (cyan) in absence of benzyl alcohol; and with 50 equiv. (dark blue) benzyl alcohol- α , α -H₂, and with 50 equiv. (green) benzyl alcohol- α , α -D₂. Black lines indicate the linear fitting of the changes over the first 500 s, see Table S3 for data.

	substrates	Rate of decrease in absorbance of Fe ^{IV} =O ($\times 10^{-5} \text{ s}^{-1}$) ^a	Rate of increase in absorbance of $Fe^{II} (\times 10^{-4} s^{-1})^{b}$
Under irradiation	benzyl alcohol- α , α -D ₂	12	7.2
	benzyl alcohol- α , α -H ₂	16	11
	cyclohexanol-D ₁₂	8.7	9.4
	cyclohexanol-H ₁₂	13	16
	No alcohol present	8.1	1.3
In dark	benzyl alcohol- α , α -D ₂	0.36	0.018
	benzyl alcohol- α , α -H ₂	2.4	0.505
	cyclohexanol-D ₁₂	0.009	<0.001
	cyclohexanol-H ₁₂	2.1	0.005
	No alcohol present	< 0.01	< 0.001

Table S3. Comparison of the rate of change of absorbance of **1** under irradiation and in the dark in acetonitrile at -30 °C with and without 50 equiv. cyclohexanol or benzyl alcohol present.

Values are obtained by linear fitting the decrease of the absorbance at 696 nm^a and 454 nm^b for the first 500 s of the reaction; see Figure S 11 and Figure S 12.





Figure S 13 ¹H NMR (600 MHz) spectra in CD₃CN of (i) A mixture of benzyl alcohol and benzaldehyde (4:1), (ii) benzyl alcohol (2.5 mM) with **1** (0.5 mM) after irradiation at 365 nm, (iii) benzyl alcohol (1.25 mM) and 1,1-D₂-benzyl alcohol (1.25 mM) and with **1** (0.5 mM) after irradiation at 365 nm, and (iv) benzyl alcohol (12.5 mM) and 1,1-D₂-benzyl alcohol (12.5 mM) and with **1** (0.5 mM) after irradiation at 365 nm. In each case, the irradiation was carried out in a 1 cm quartz cuvette with monitoring by UV/Vis absorption spectroscopy. Irradiation was stopped, 1 mL of the solution passed through a plug of silica to remove **1a** and the ¹H NMR spectra recorded after the absorbance at 696 nm reached zero.



Figure S 14. (left) UV-vis absorption spectrum of 1 (0.5 mM) in CH₃OH at -30 °C before (black) and during irradiation at 365 nm (dashed lines) with the final spectrum in red. Inset is the expansion at range 500 to 900 nm. (Right) the corresponding absorbance changes at 692 nm (solid squares, left y-axis) and 458 nm (open squares, right y-axis) over time. Irradiation was commenced at 600 s.



Figure S 15. Comparison of normalized absorbance of **1** (0.5 mM) in CH₃OH (black) and in CD₃OD (red) at (left) 458 nm and (right) 692 nm over time at -30 $^{\circ}$ C during irradiation at 365 nm.

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