Supporting Information for:

Determining the Fate of a Non-heme Iron Oxidation Catalyst Under Illumination, Oxygen, and Acid
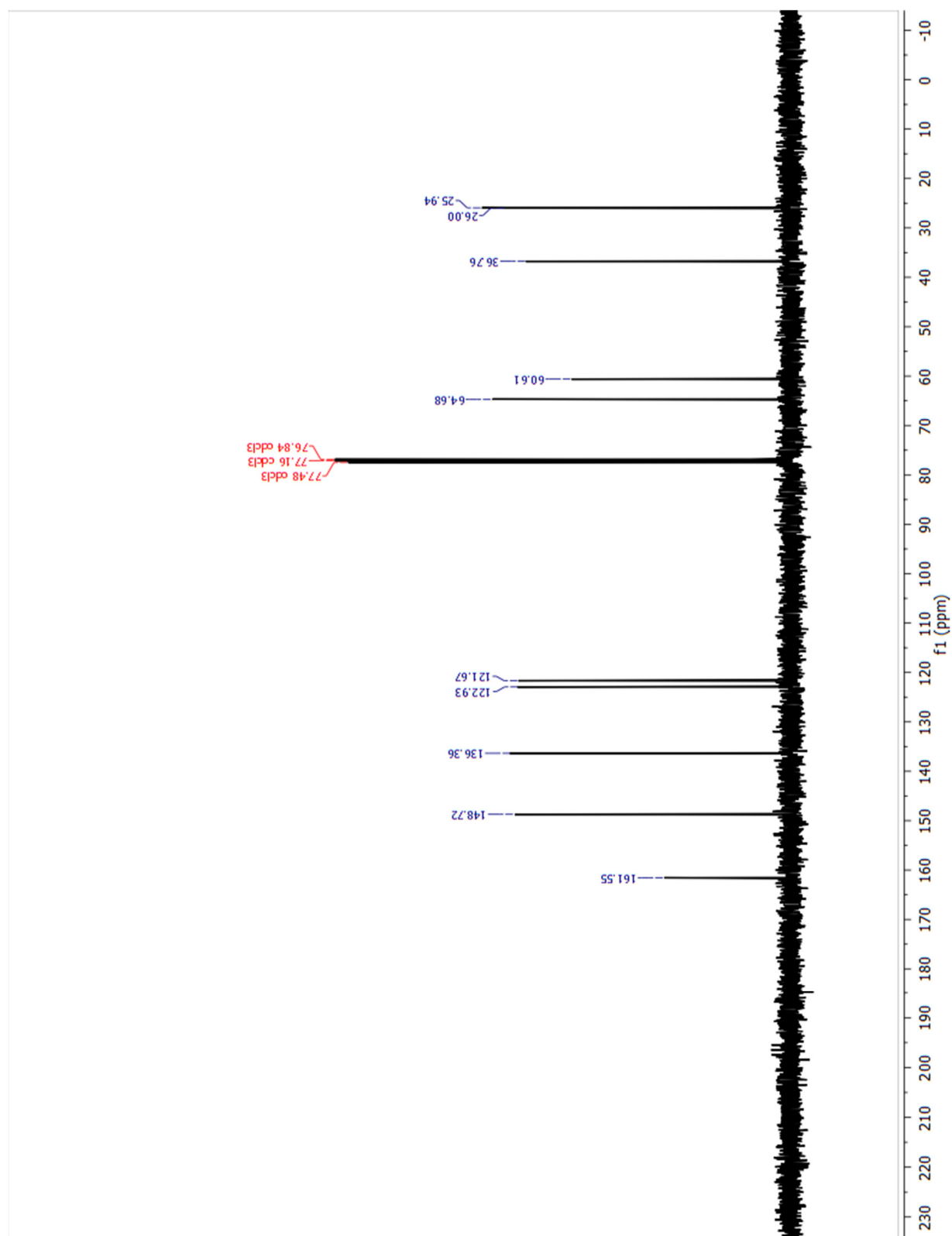
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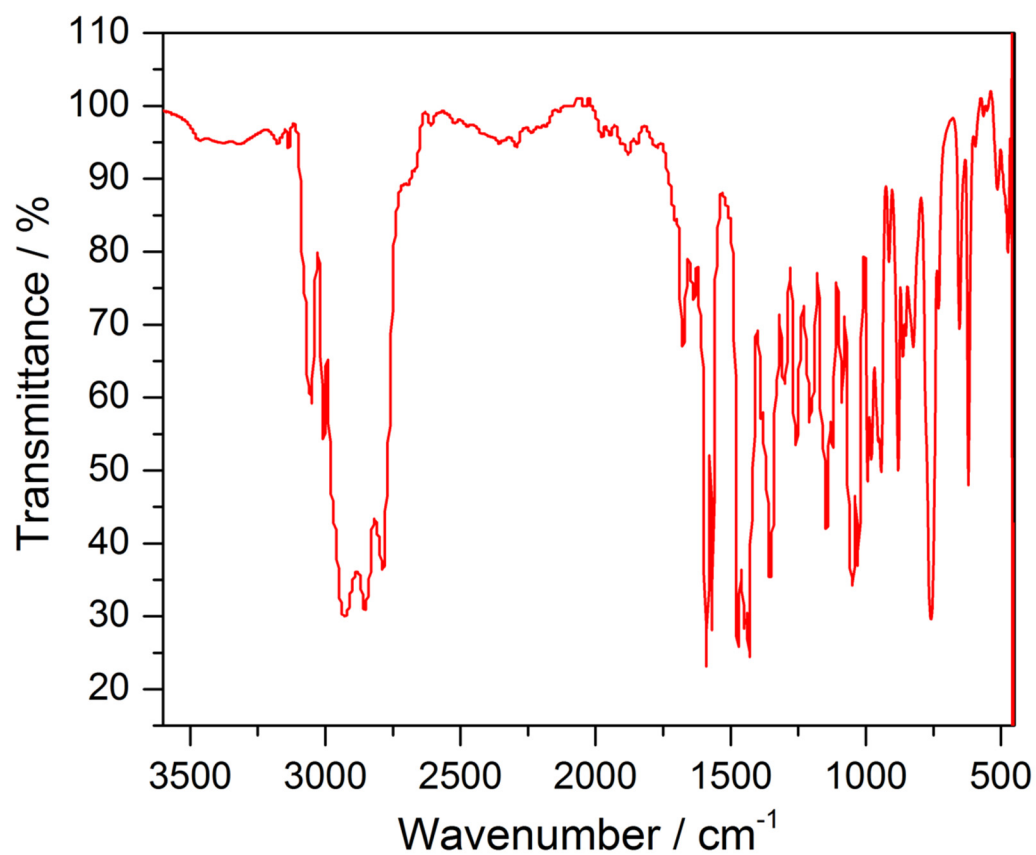
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Figure S1. ^{1}H NMR spectrum of bpmcn ligand in CDCl$_3$

Figure S2. ^{13}C NMR spectrum of bpmcn ligand in CDCl$_3$

Figure S3. FTIR spectrum of the bpmcn ligand
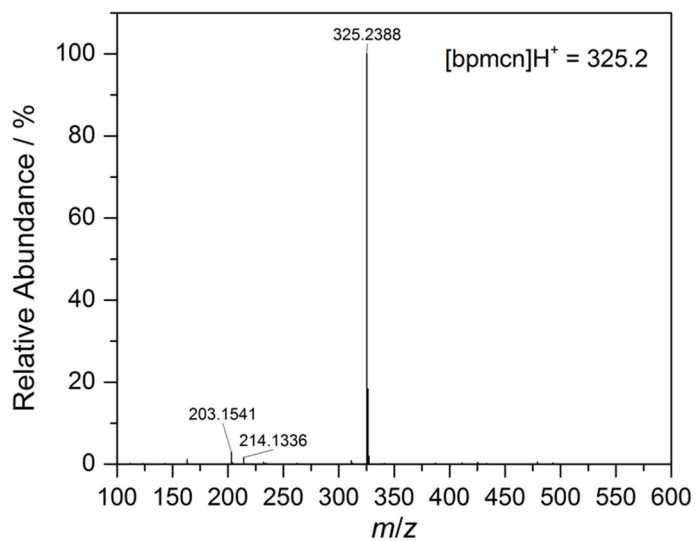
Figure S4. ESI-MS(+) spectrum of purified bpmcn ligand
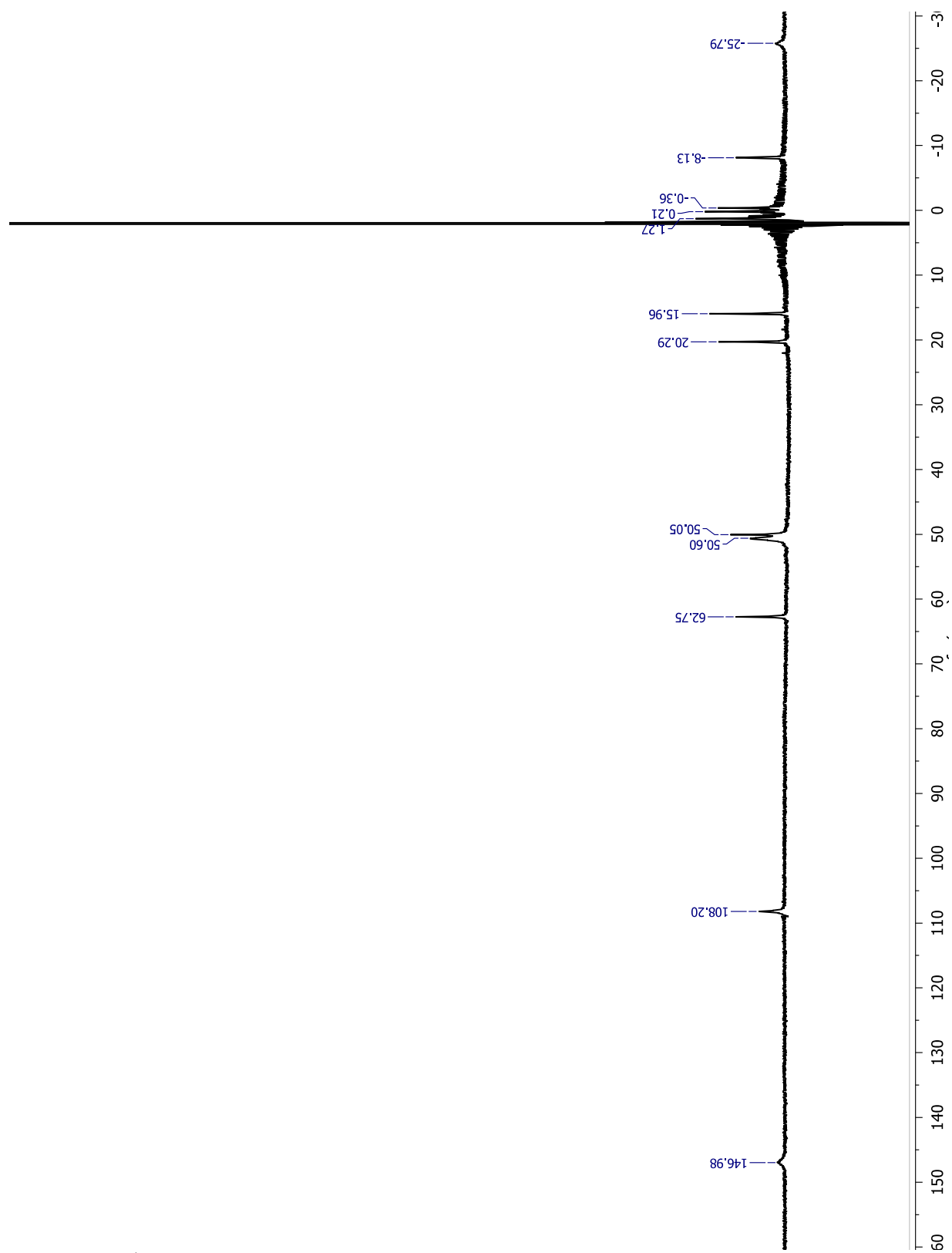
Figure S5. ^1H NMR spectrum of Fe(bpmcn)Cl$_2$ in CD$_3$CN
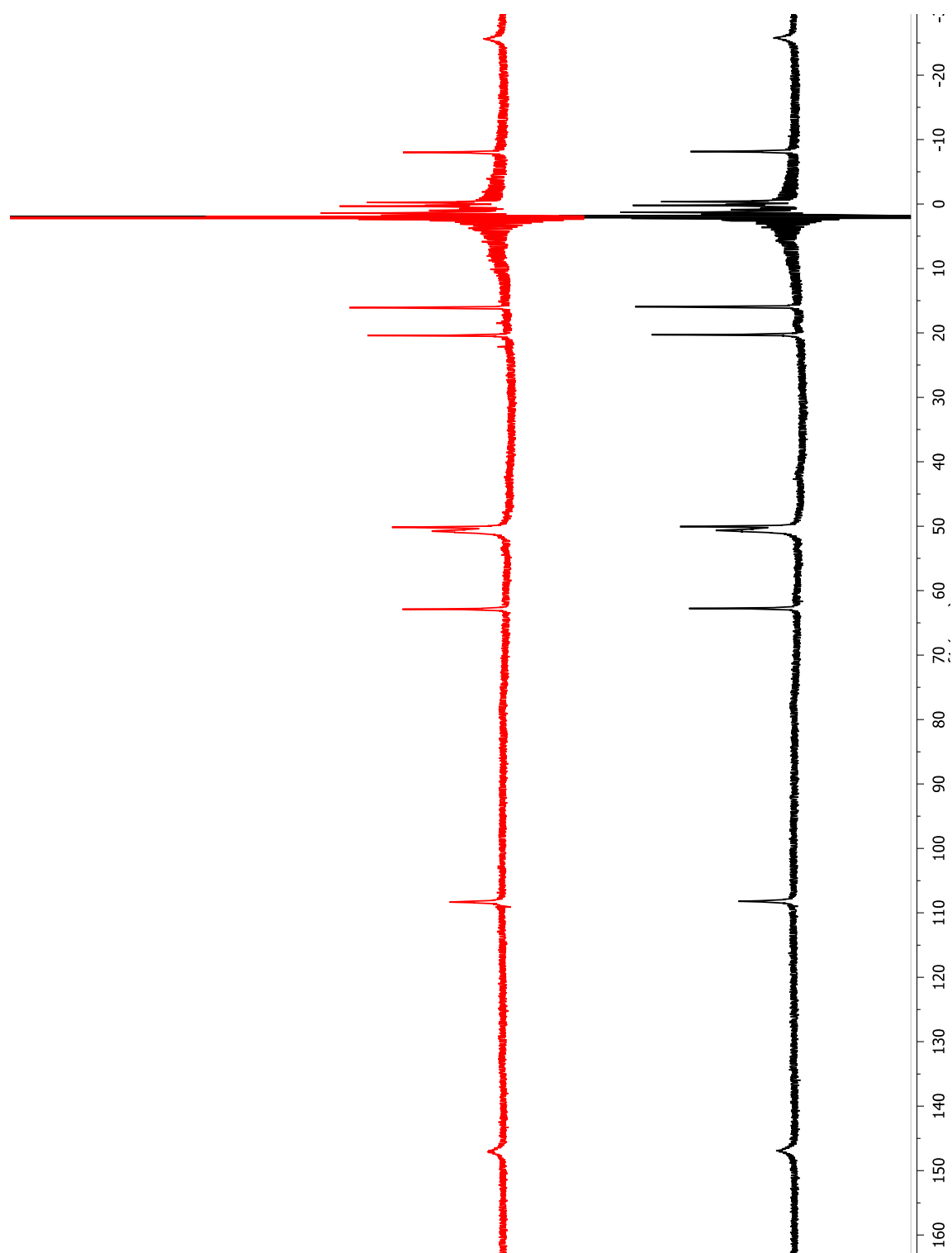
Figure S6. ^{1}H NMR spectra of a solution of Fe(bpmcn)Cl$_2$ in dry d_3-CD$_3$CN under N$_2$ (black) in the dark and (red) under 1 sun of illumination for t = 24 hours.
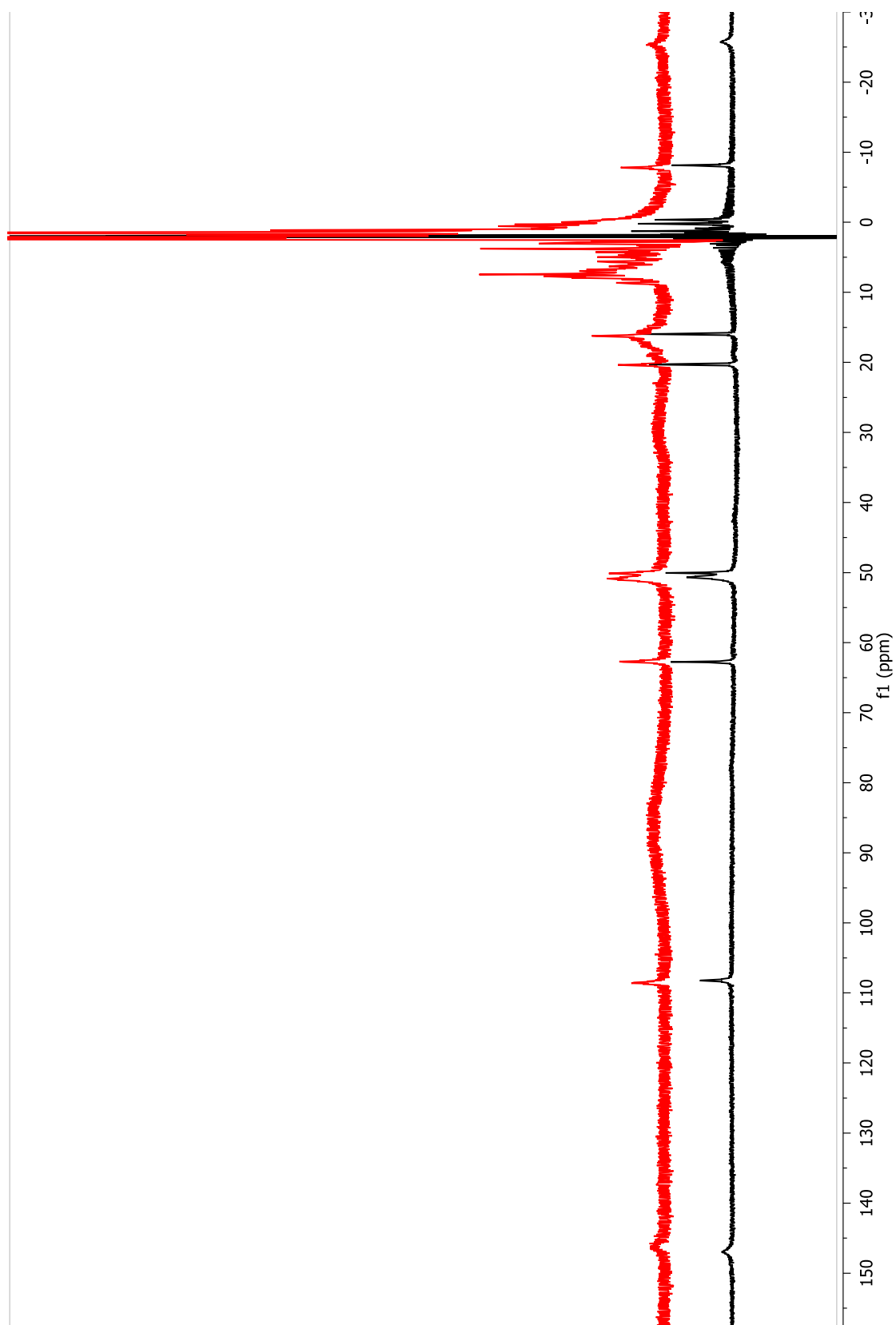
Figure S7. ^{1}H NMR spectra of Fe(bpmcn)Cl$_2$ (black) in the dark and (red) after exposure of 1 sun illumination under O$_2$ for 24 hours in dry acetonitrile.
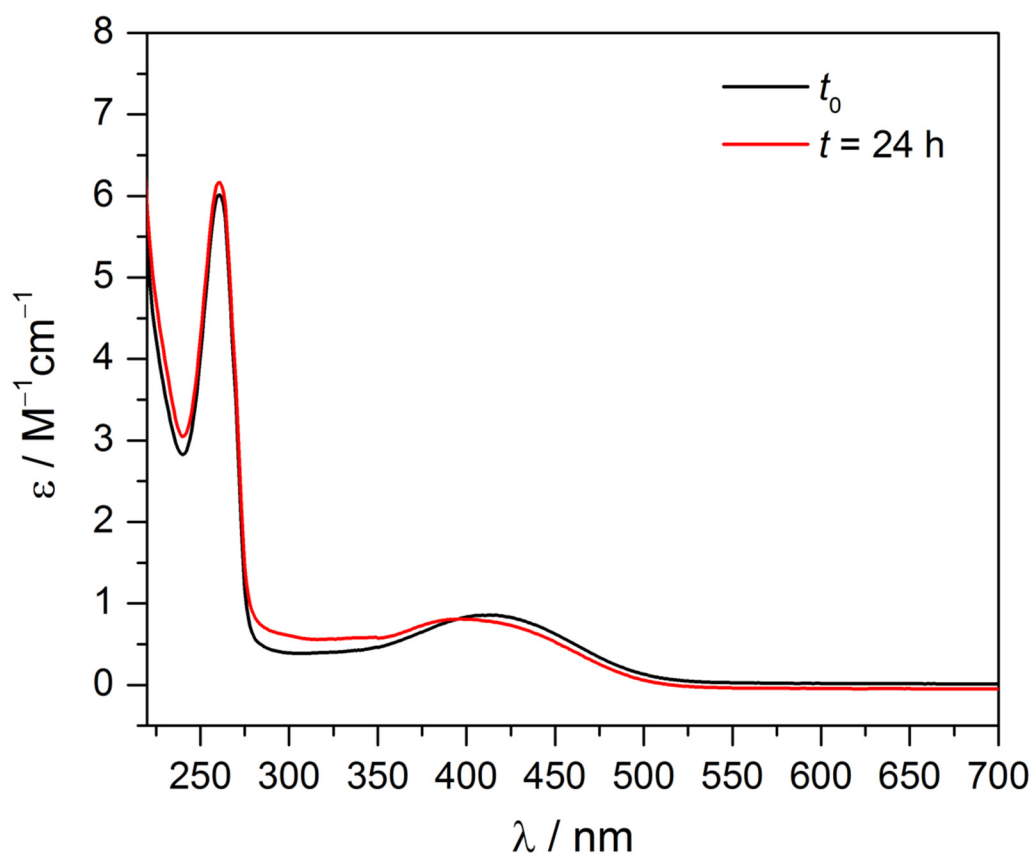
Figure S8. UV-Vis spectra of Fe(bpmcn)Cl$_2$ under O$_2$ (black) in the dark and (red) under illumination at 1.5 W with a Xe lamp and 550 nm cutoff filter equipped.
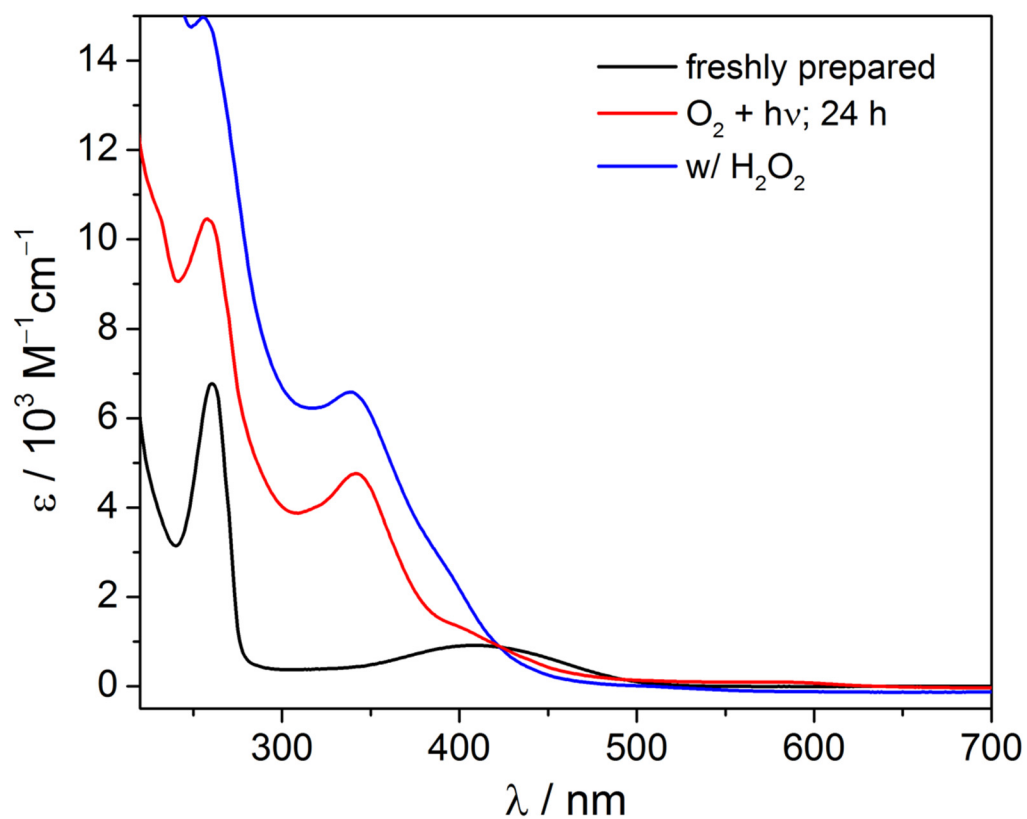
Figure S9. UV-Vis spectrum of 0.2mM Fe(bpmcn)Cl$_2$ (black) prior to and (red) after adding 5 μL of 30 wt-wt% H$_2$O$_2$ (added to a 10 mL solution of the iron complex), compared to (blue) 0.2 mM Fe(bpmcn)Cl$_2$ under 1 sun illumination for 24 hours.
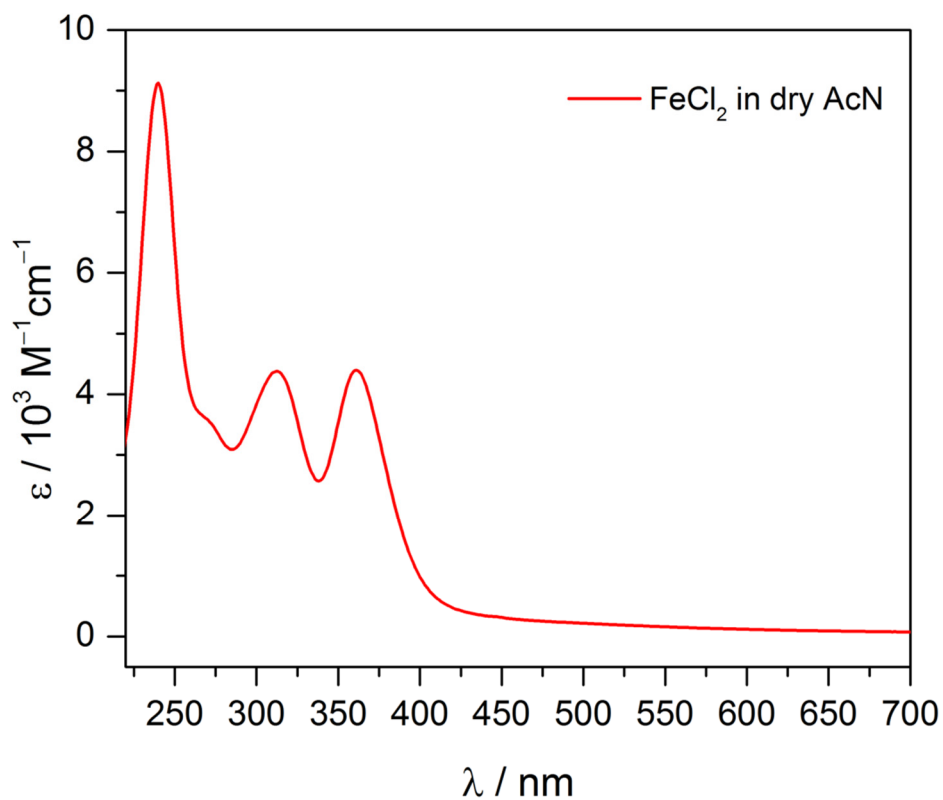
Figure S10. UV-Vis spectrum of $FeCl_2$ in dry acetonitrile under N_2. In dry acetonitrile, absorption bands appear for $FeCl_2$ at λ_{max} = 240 nm, λ_{max} = 312 nm, and λ_{max} = 361 nm
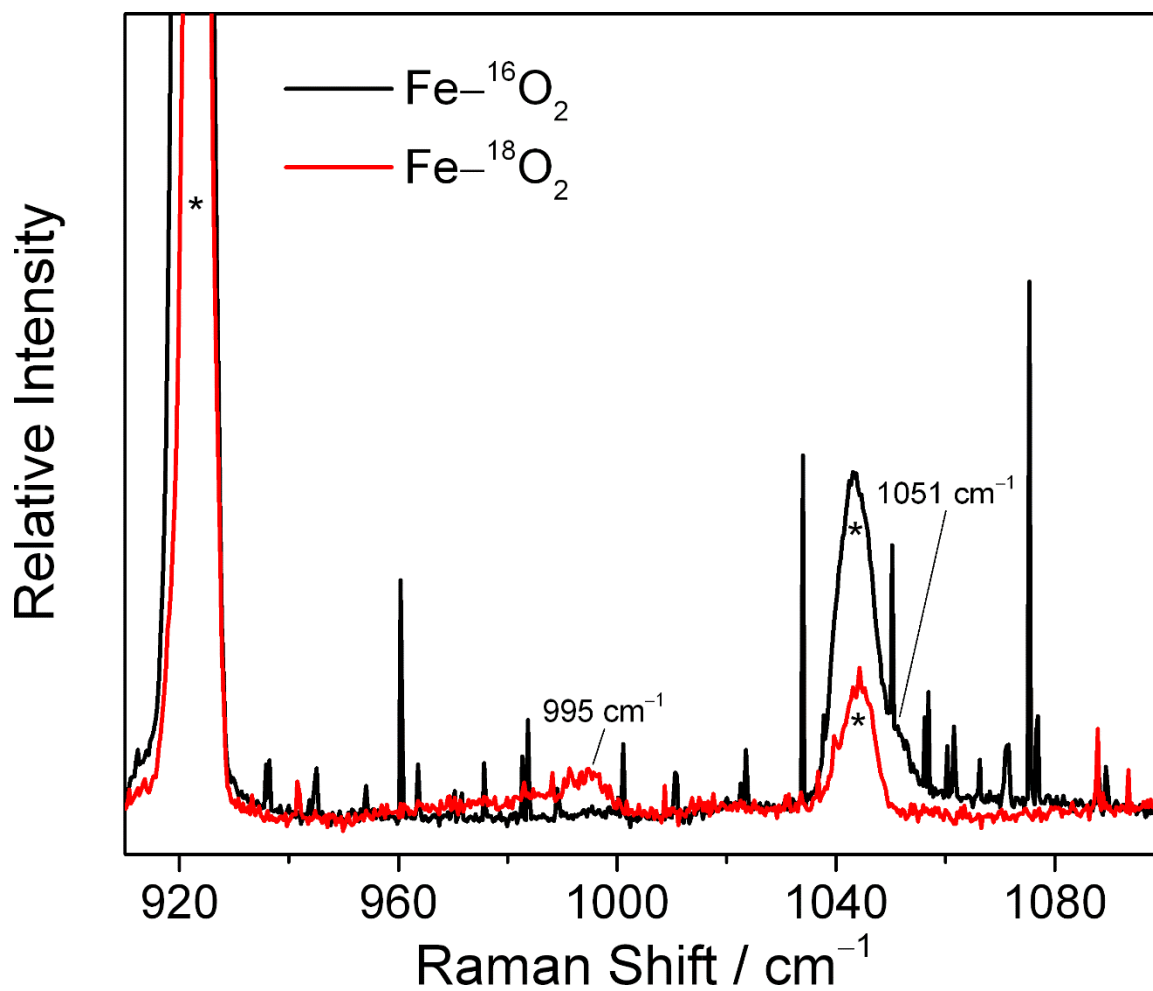
Figure S11. Raw resonance Raman spectra of Fe–$^{32}O_2$ (black) and Fe–$^{36}O_2$ (red) in dry acetonitrile, including cosmic rays detected by the detector. Solvent peaks are denoted with an asterisk.
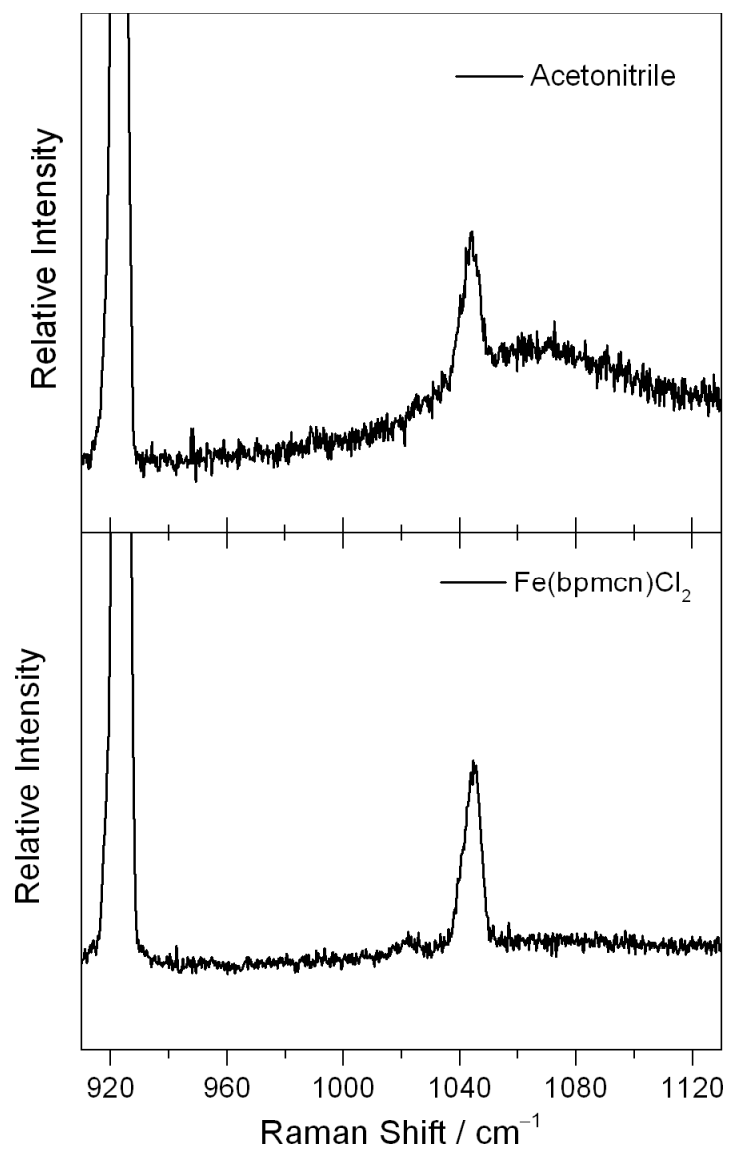
Figure S12. Resonance Raman spectra of (a) dry acetonitrile, and (b) Fe(bpmcn)Cl₂ in dry acetonitrile recorded at 77 K with 413 nm laser.
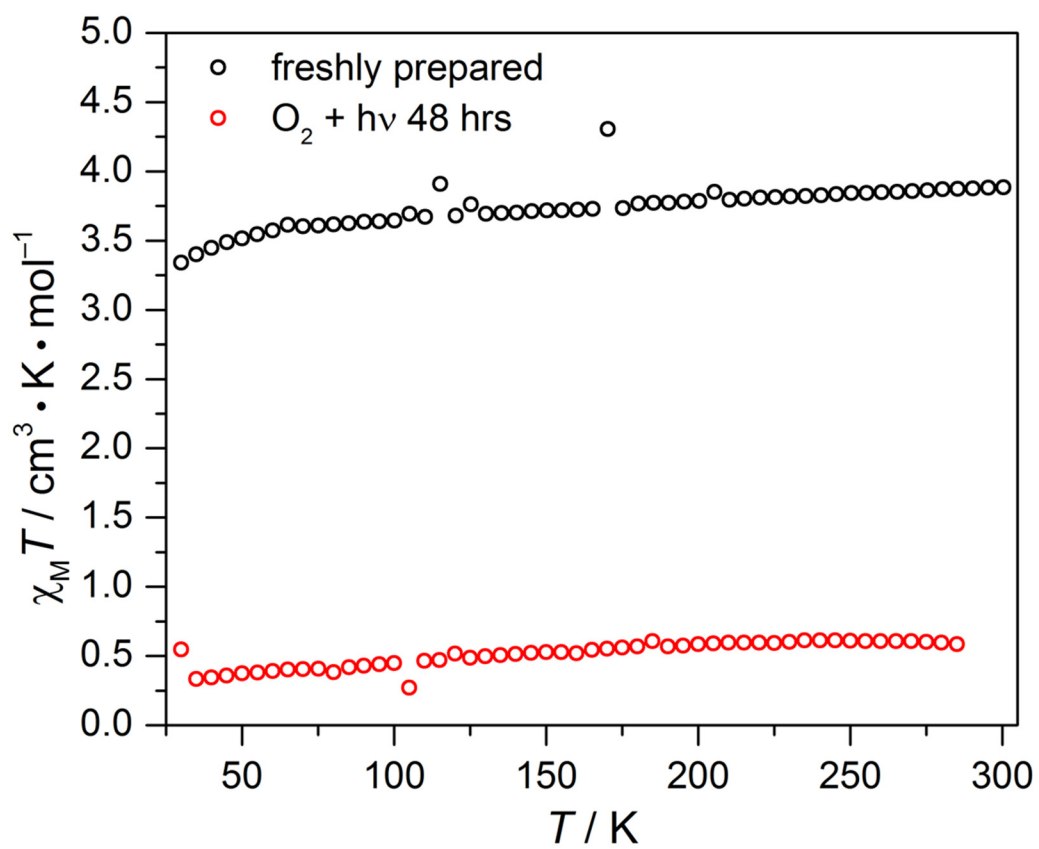
Figure S13. Variable-temperature magnetic susceptibility of Fe(bpmcn)Cl₂ (black) pre- and (red) post-exposure to O₂ under 1.5 W of illumination through an AM 1.5G filter.
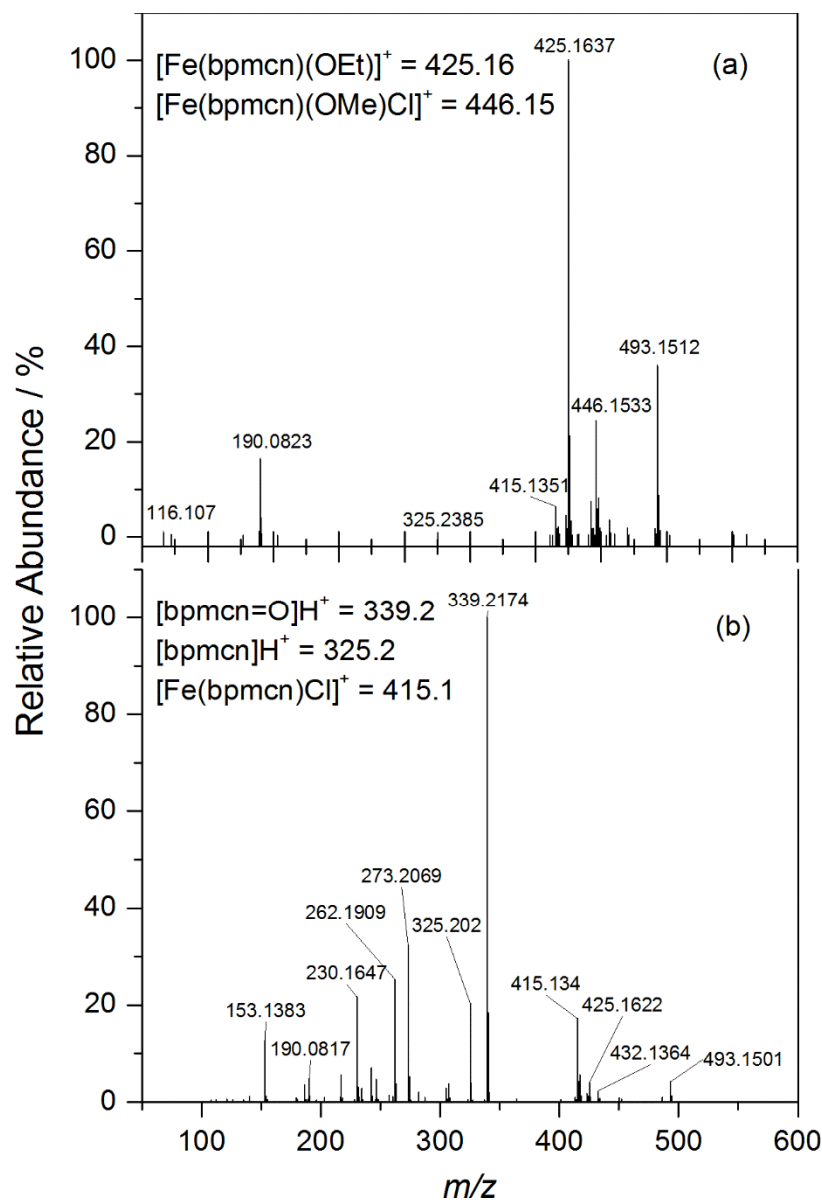
Figure S14. ESI-MS$^+$ spectra of Fe(bpmcn)Cl$_2$ (a) prior to and (b) after exposure to 1.5 W illumination with AM 1.5G filter for 48 hours under O$_2$.
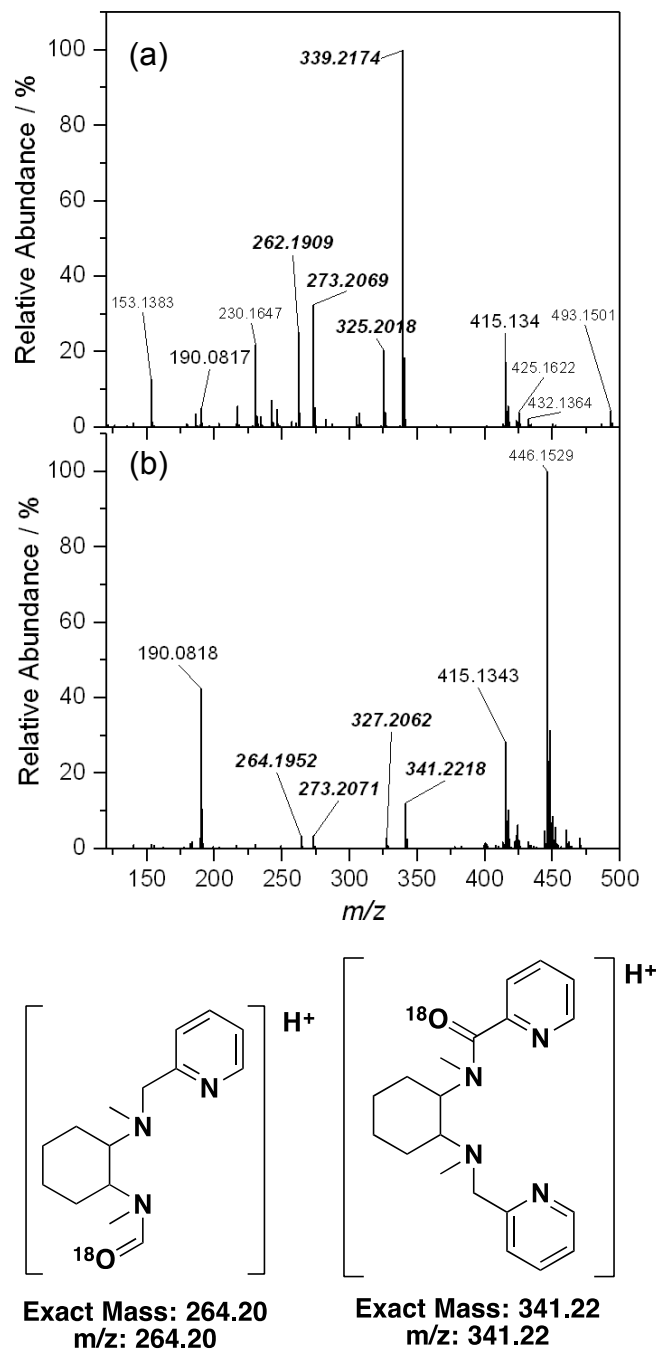
Figure S15. ESI-MS$^+$ spectra of Fe(bpmcn)Cl$_2$ exposed to 1.5 W illumination with AM 1.5G filter for 48 hours under (a) ^{32}O$_2$ or (b) ^{36}O$_2$
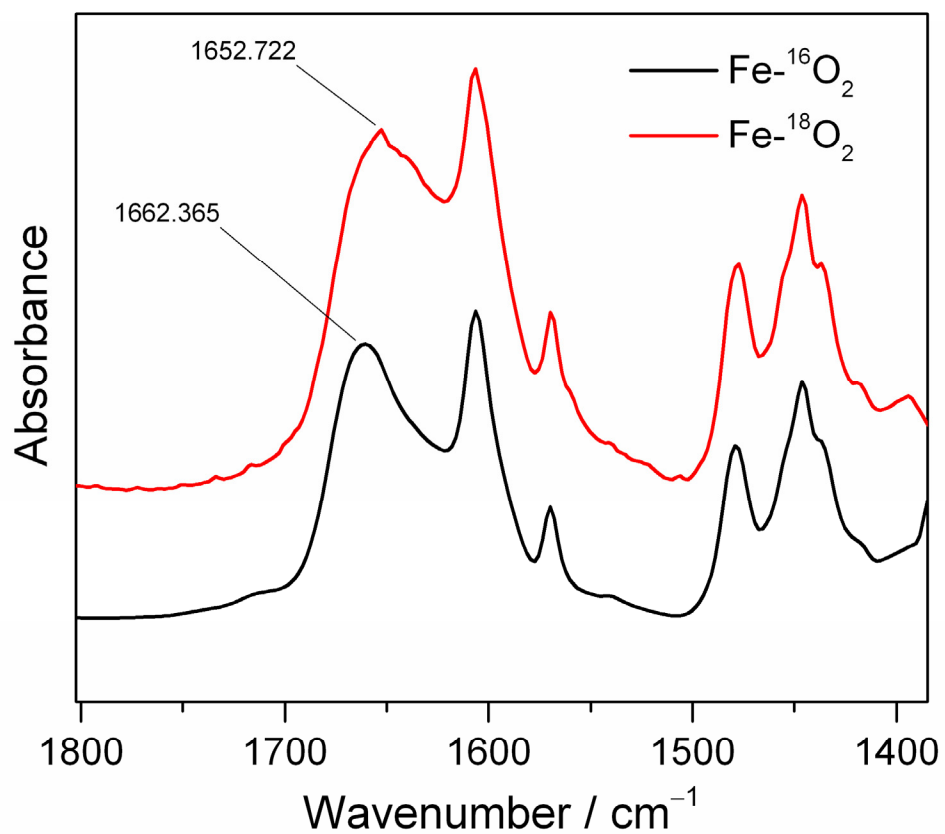
Figure S16. FTIR spectra of Fe(bpmcn)Cl$_2$ after illumination with 1.5W through an AM 1.5G filter in acetonitrile under (black) $^{32}O_2$ and (red) $^{36}O_2$. Note the region between 1600 – 1700 cm^{-1} where an amide bond typically appears in the IR spectrum.

(a)
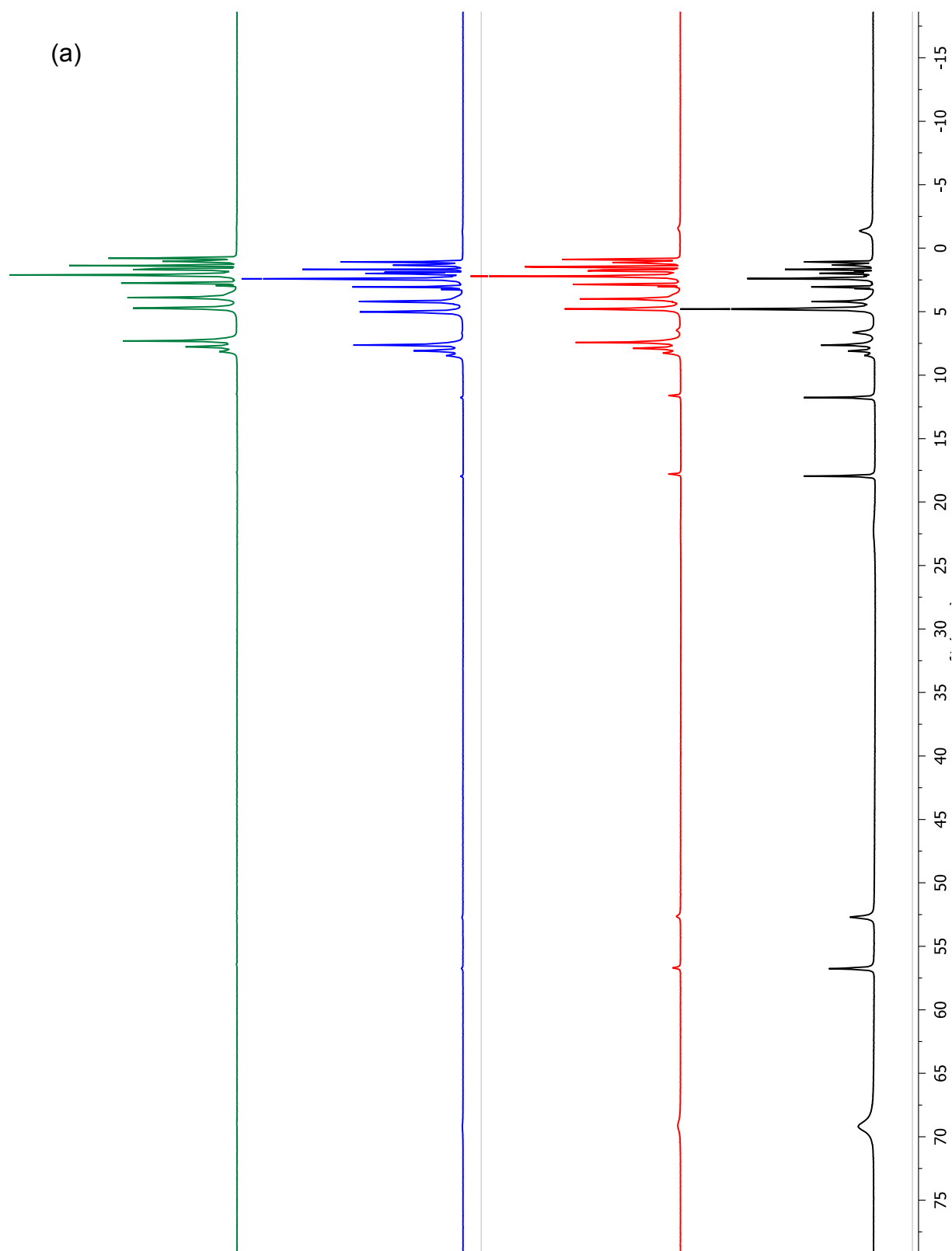
Figure S17. ^1H NMR spectra of a solution of Fe(bpmcn)Cl$_2$ in degassed D$_2$O with 0.1 M d-TFA (pH = 1) in the dark for t=0 minutes (black), 2 hours (red), 4 hours (blue), and 8 hours (green).

(b)
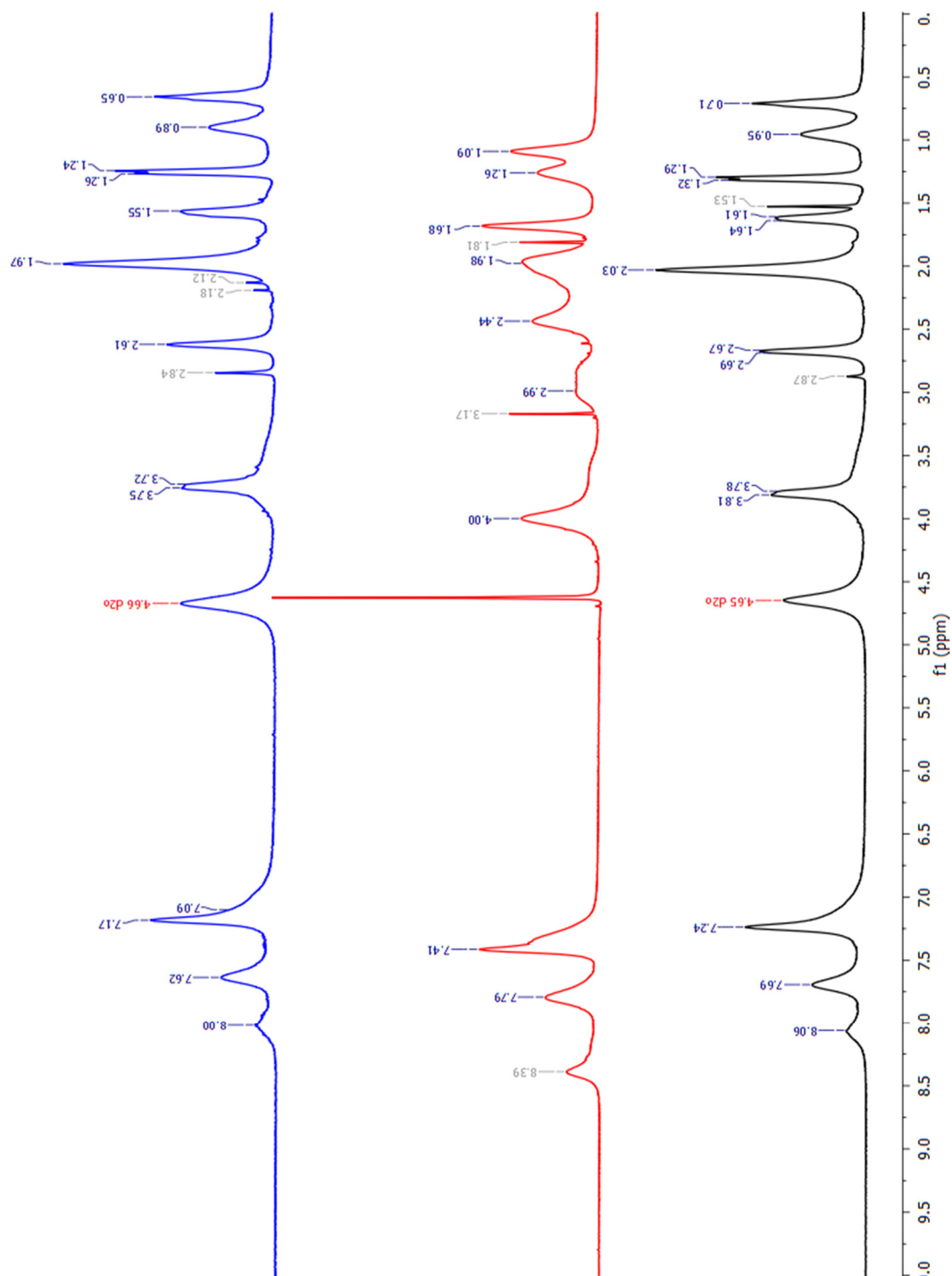
Figure S18 ^{1}H NMR spectra of (black) Fe(bpmcn)Cl$_2$ in 0.1 M *d*-TFA for 8 hours, (red) free bpmcn in 0.1M *d*-TFA, and (blue) FeCl$_2$ + bpmcn in 0.1M *d*-TFA.
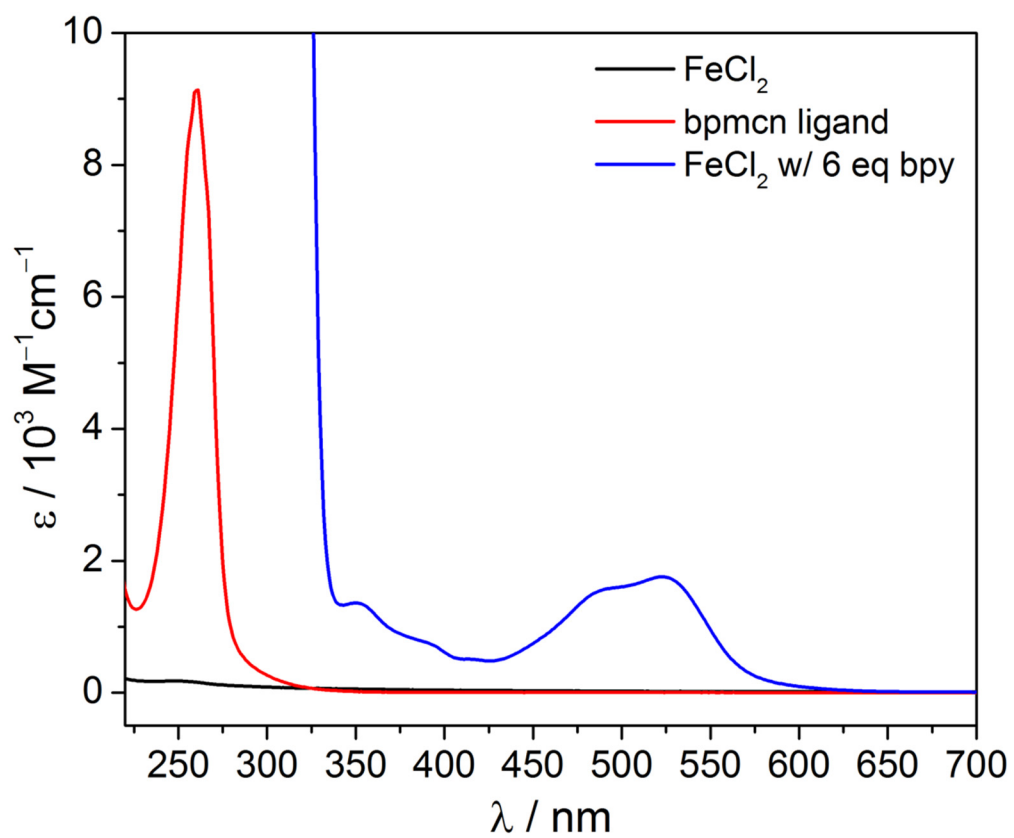
Figure S19. UV-Vis spectrum of (black) $FeCl_2(aq)$, (red) bpmcn ligand, and (blue) $FeCl_2$ with 6 equivalents of 2,2′ bpy in TfOH at pH 1 under N_2.
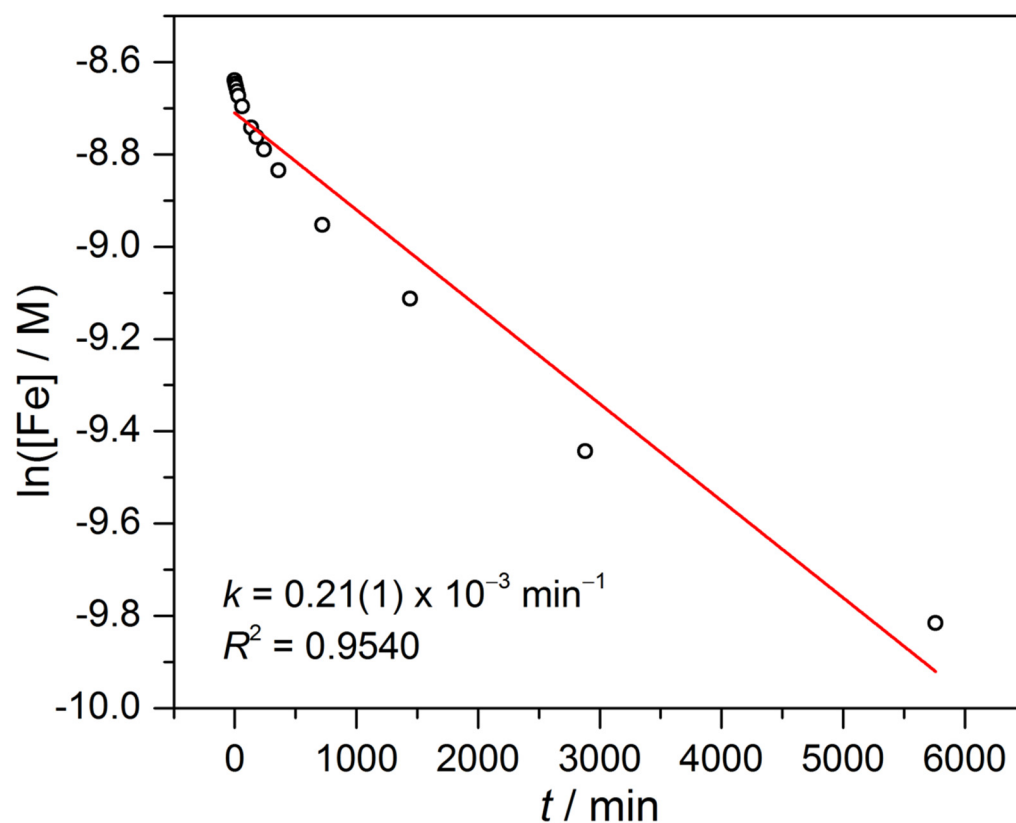
Figure S20. ln([Fe]) vs time of the λ_{max} = 364 nm absorption of Fe(bpmcn)Cl$_2$ (Fe) in pH 3 TfOH under N$_2$ over 4 days. Linear fitting: ln([Fe]) = -0.00021t – 8.709; R^2 = 0.9540. The data deviate significantly from first-order kinetics after 1 h.
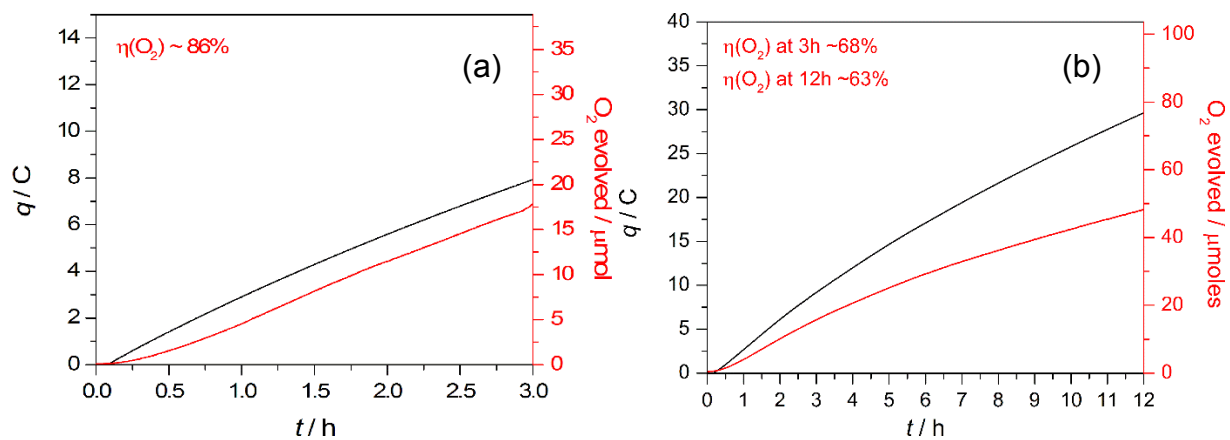
Figure S21. OER data collected of an **Fe**|WO$_3$ electrode in 100 mM NaSO$_4$ pH 3 during bulk electrolysis held at 1.23 V vs RHE, SCE RE, Pt CE for 12 hours with charged passed (black) and oxygen evolved (red). Reproduced with permission from ref. 19. Copyright 2014 American Chemical Society.