

Supplementary Information

Elucidating the Mechanism of Photochemical CO₂ Reduction to CO Using a Cyanide-Bridged Di-Manganese Complex

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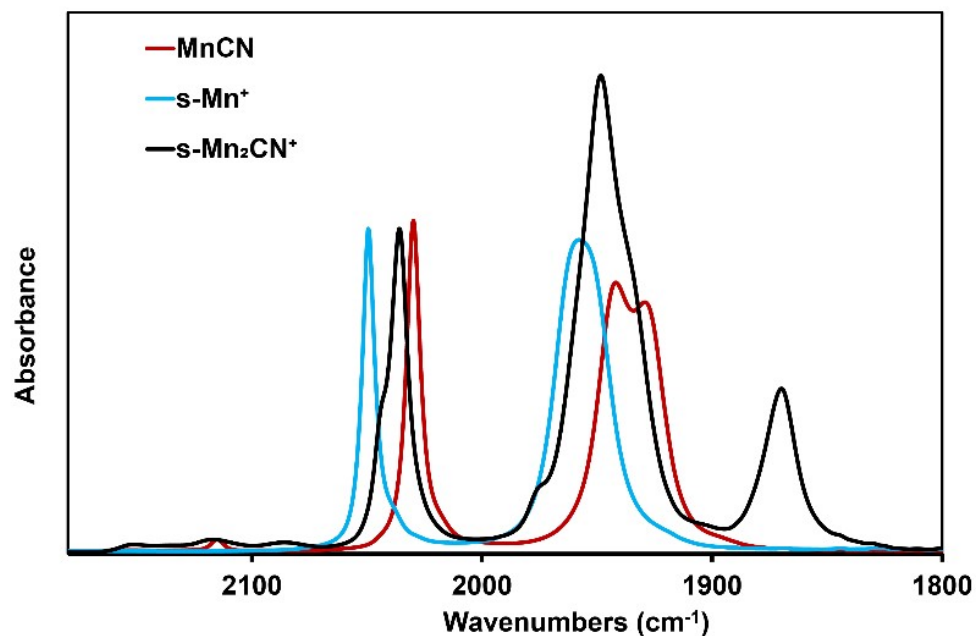


Figure S1. The liquid phase IR spectrum of $s\text{-Mn}_2\text{CN}^+$ compared with those of $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{MeCN})](\text{PF}_6)$ (blue) and $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{CN})]$ (red).

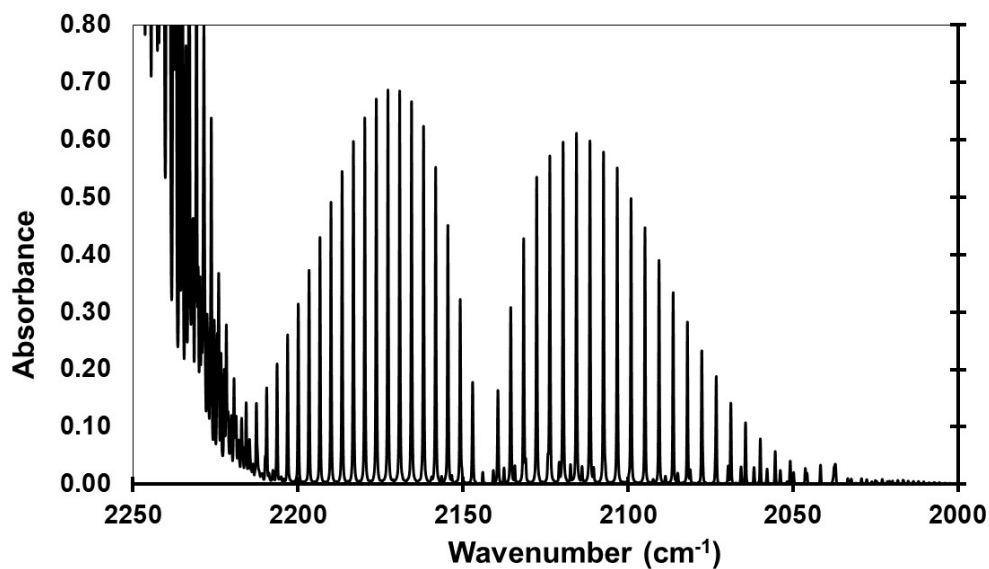


Figure S2. Headspace gas infrared spectrum of 1 mM Mn_2CN^+ with 1 M phenol after irradiation with 395 nm LED for 1 h. The ratio of $^{13}\text{CO}/^{12}\text{CO}$ is 5%.

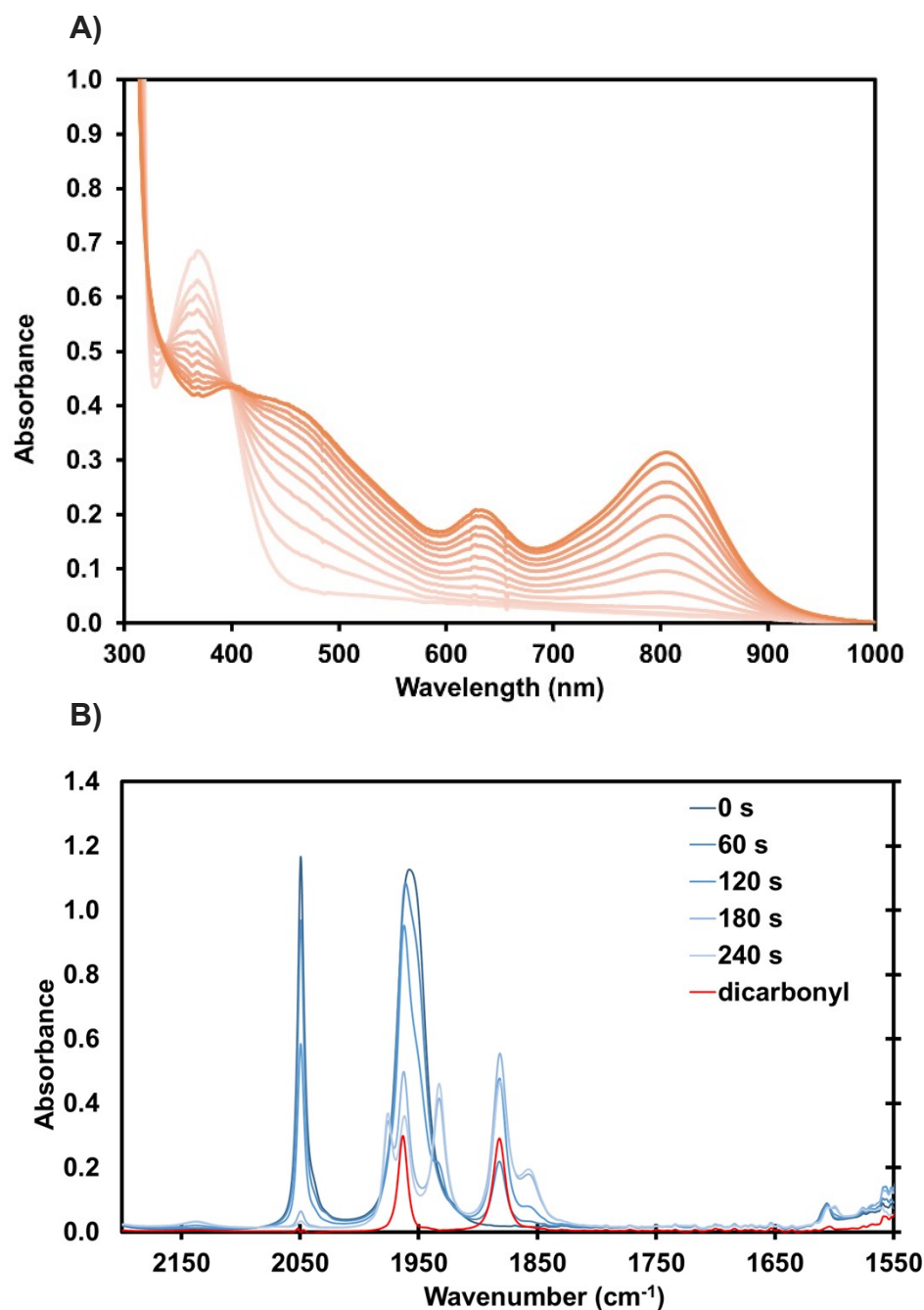


Figure S3. A) UV-vis spectra of 0.33 mM $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{MeCN})]^+$ in degassed MeCN taken every 10 s of irradiation at 395 nm, showing a decrease in $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{MeCN})]^+$ at 375 nm and an increase in the dicarbonyl species, $[\text{Mn}(\text{bpy})(\text{CO})_2(\text{MeCN})_2]^+$ (shoulder ~ 500 nm) for the first 20 s. From 30 to 110 s, **Mn-Mn** is detected. B) Liquid IR spectra of 10 mM $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{MeCN})]^+$ in degassed MeCN, taken every 60 s of irradiation at 395 nm. The dicarbonyl signal (red) is the initial signal subtracted from the signal at 60 s, showing two peaks at 1960 and 1880 cm^{-1} .

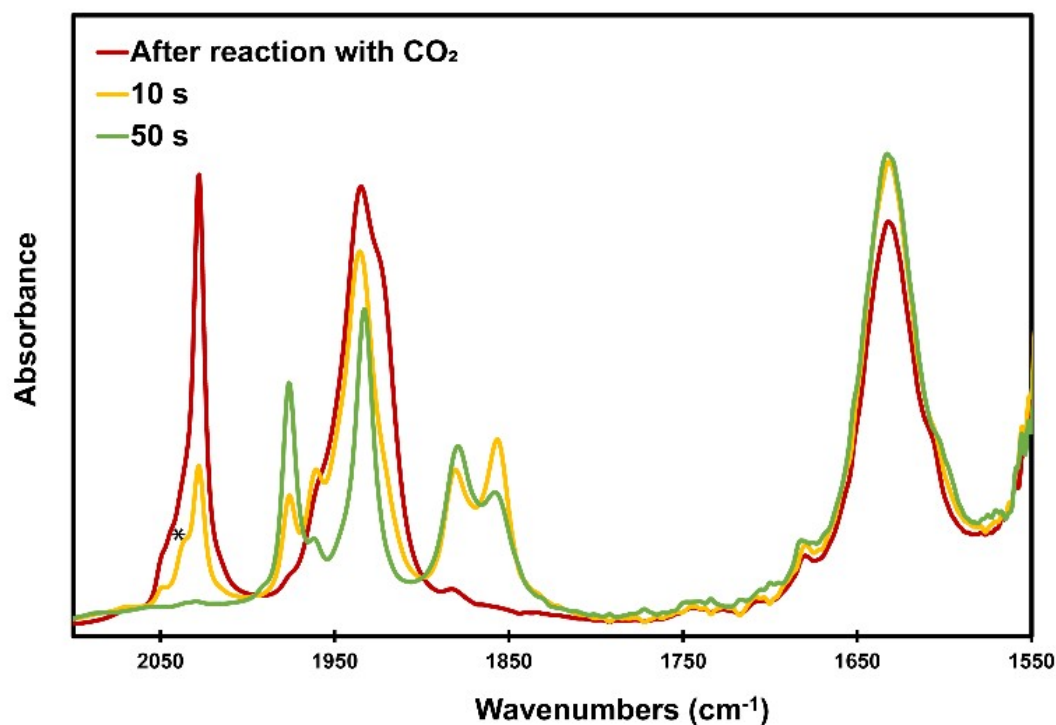


Figure S4. Liquid phase IR spectra immediately after **Mn-Mn** in degassed MeCN was combined with CO₂-saturated MeCN in the dark (red), and then after irradiation with 395 nm light. *indicates an axial carbonyl peak.

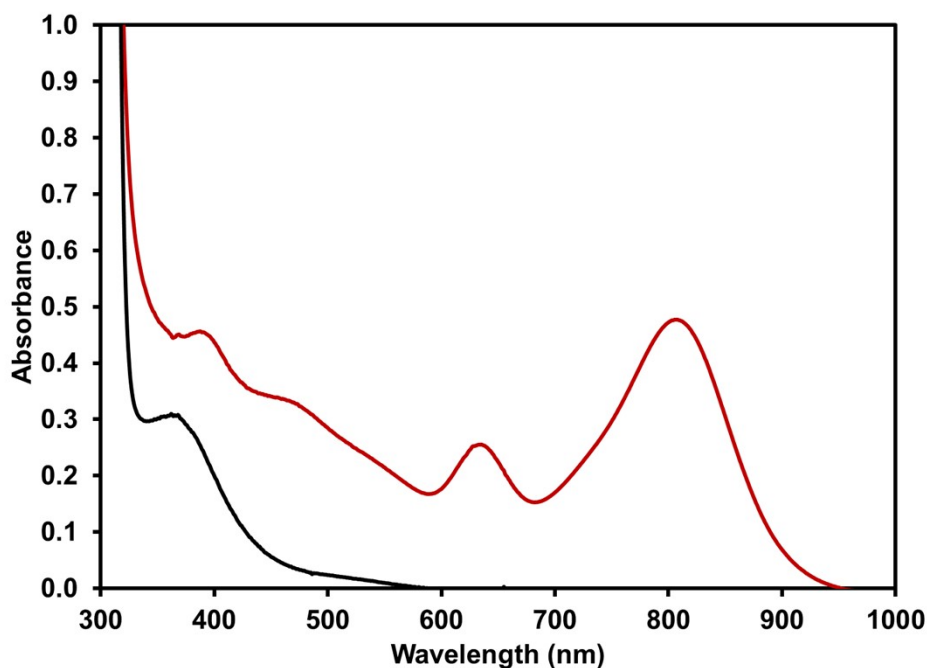


Figure S5. UV-vis of 0.04 mM **Mn-Mn** and 1 M PhOH in degassed MeCN (red). After the introduction of CO₂, two peaks at 375 and a shoulder ~500 nm corresponding to [Mn(bpy)(CO)₃(MeCN)]⁺ and [Mn(bpy)(CO)₂(MeCN)₂]⁺, respectively, persist in solution.

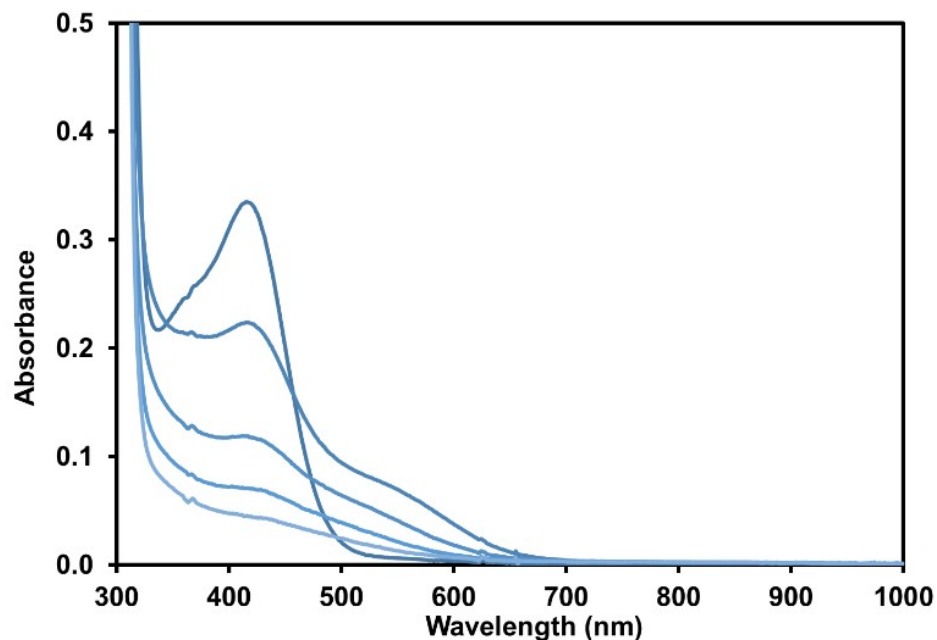


Figure S6. UV-vis of 0.087 mM $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ and 10 mM PhOH in CO_2 -saturated MeCN every 60 s of irradiation at 395 nm, showing a decrease in the *fac* isomer and an increase in the *mer* isomer (shoulder ~ 570 nm.) No **Mn-Mn** was detected.

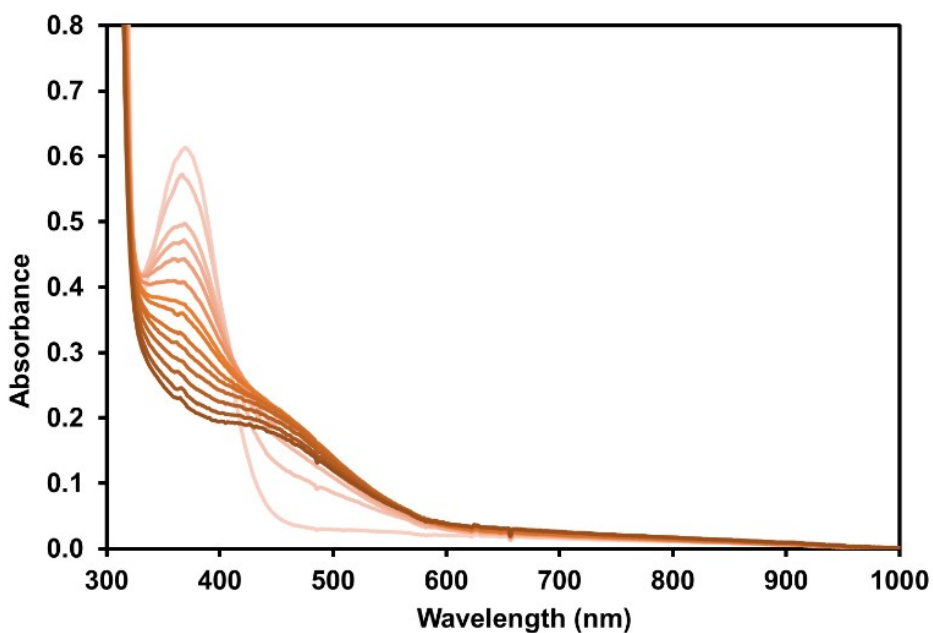


Figure S7. UV-vis of 0.33 mM $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{MeCN})]^+$ in CO_2 -saturated MeCN every 10 s of irradiation at 395 nm, showing a decrease in $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{MeCN})]^+$ at 375 nm and an increase in the dicarbonyl species, $[\text{Mn}(\text{bpy})(\text{CO})_2(\text{MeCN})_2]^+$ (shoulder ~ 500 nm). No **Mn-Mn** was detected.

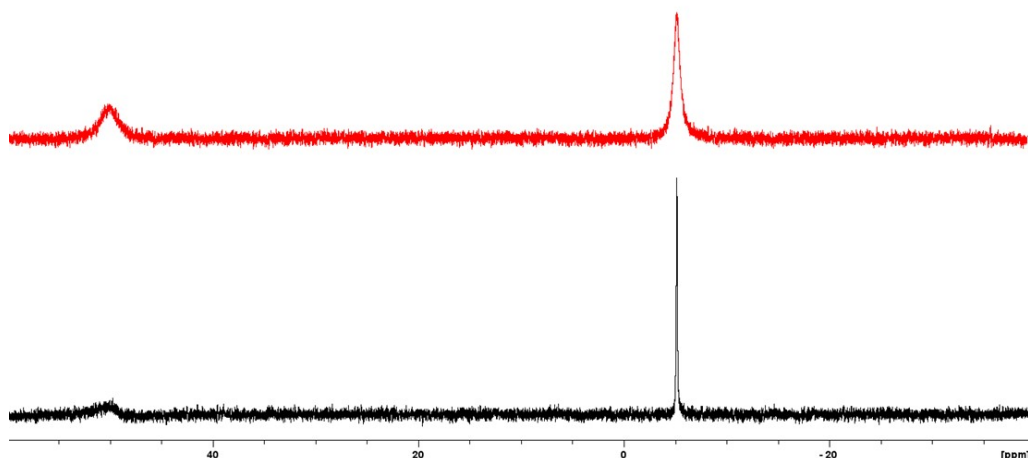


Figure S8. ^{31}P NMR of 15.26 mM PPh_3 and 14 mM $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{MeCN})]^+$ (red) and 15.26 mM PPh_3 and 14 mM **Mn-Mn** (black). Free PPh_3 is located at -5.14 ppm and ligated PPh_3 is located at 49.75 ppm. ^{31}P NMR spectra were referenced to 85% H_3PO_4 solution as an external standard in d-MeCN.

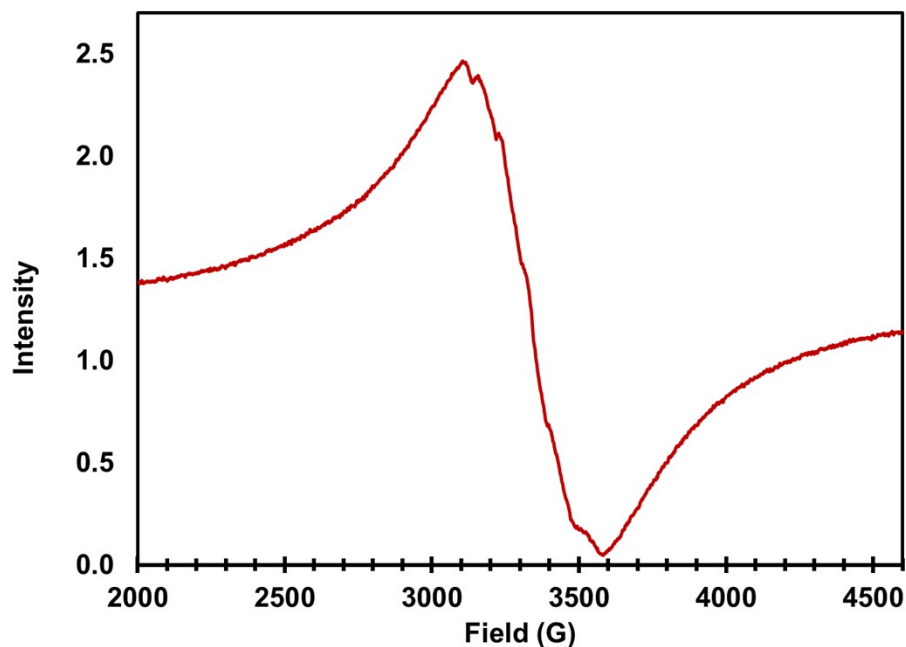


Figure S9. X-band EPR spectrum (10 K) of **Mn-Mn** in degassed MeCN upon addition of CO_2 in the dark, followed by freezing at 4 K. The EPR signal ($g = 2.001$) is indicative of a Mn^{II} species.

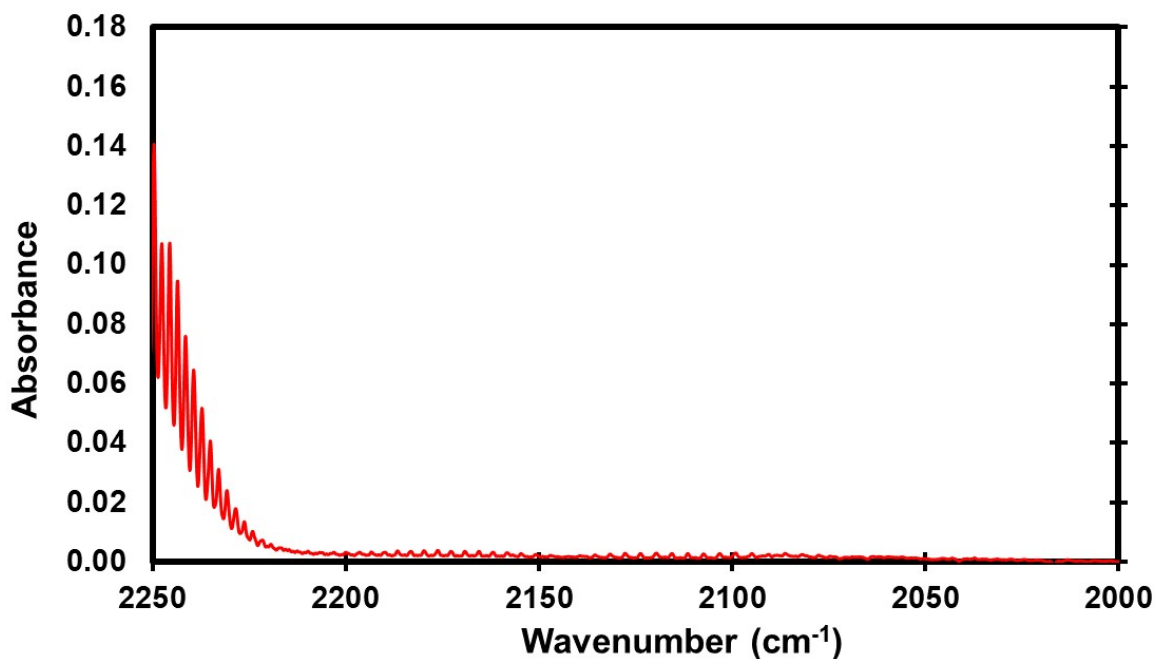


Figure S10. Headspace gas infrared spectra of ~ 6.5 mM **Mn-Mn** with 1 M phenol before irradiation with 395 nm LED for 3 h, showing no detectable CO in the headspace.

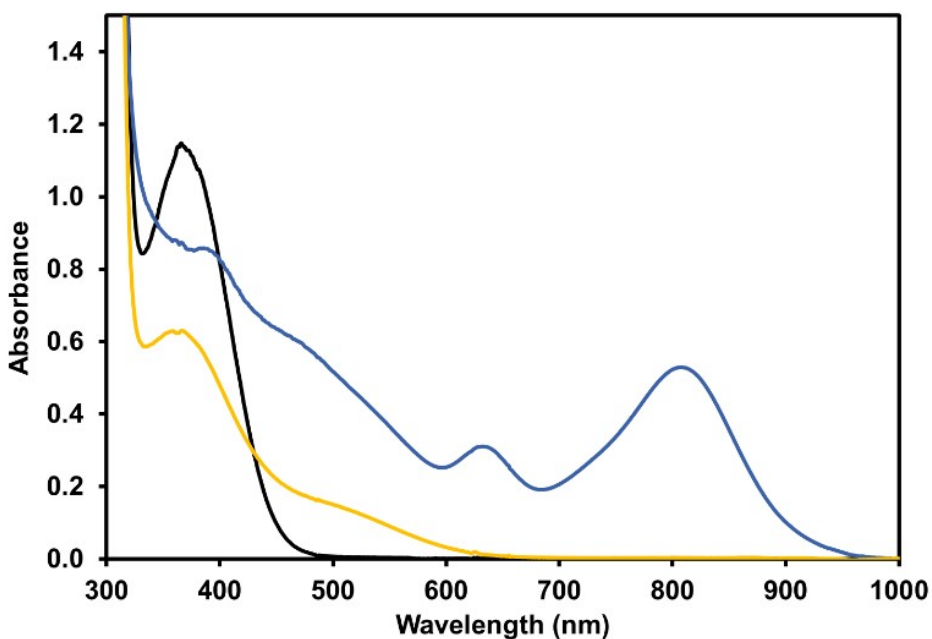


Figure S11. UV-vis of 0.1 mM **Mn₂CN⁺** and 1 M PhOH in degassed MeCN (yellow) after irradiation for 300 s at 395 nm (blue) showing **Mn-Mn** formation. After the introduction of CO₂, two peaks at 375 and a shoulder ~ 500 nm corresponding to $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{MeCN})]^+$ and $[\text{Mn}(\text{bpy})(\text{CO})_2(\text{MeCN})_2]^+$, respectively, persist in solution.

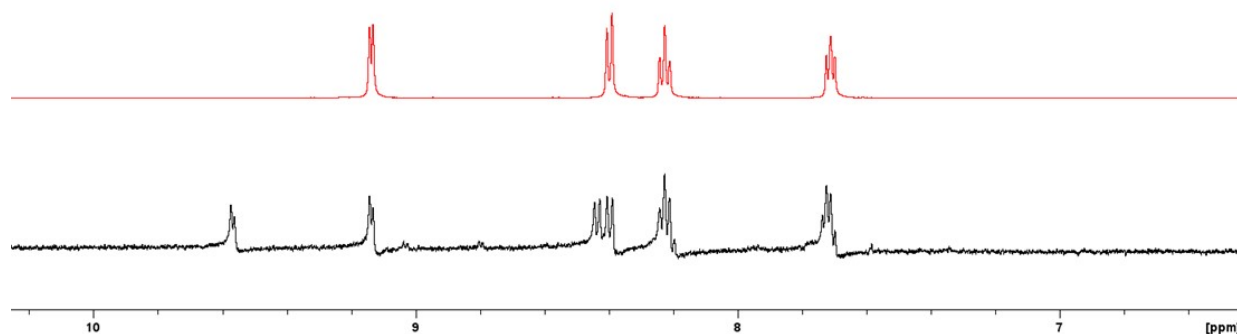


Figure S12. ^1H NMR of $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{MeCN})]^+$ (red) and $[\text{Mn}(\text{bpy})(\text{CO})_2(\text{MeCN})_2]^+$ (black) in d-MeCN.

Quantum Yield Calculation:

$$\text{Quantum Yield} = \left(\frac{\text{mol CO}}{(\text{light absorbed, } W)(\text{irradiation time, } s)} \right) \frac{1}{(\text{energy per Einstein})}$$

$$0.64 = \left(\frac{4.98 \times 10^{-6} \text{ mol CO}}{(0.00130 \text{ J/s})(1800 \text{ s})} \right) \frac{1}{\left(\frac{hc}{395 \times 10^{-9} \text{ m}} \right) N_A}$$

Intensity absorbed = 1.30 mW @ 395 nm

Energy per Einstein = $(hc/395 \text{ E}^{-9} \text{ m}) \cdot N_A$

N_A = Avogadro's number

Irradiation time = 1800 s

Table S1. IR shifts of common Mn and Re complexes

Mn Complex	CO stretches and OCO stretches denoted with * (cm ⁻¹) exptl.	CO stretches (cm ⁻¹) exptl. calc.	Solvent	Ref.
<i>fac</i> -Mn(bpy)(CO) ₃ CN	2030, 1941, 1934		MeCN	1
<i>fac</i> -Mn(bpy)(CO) ₃ Cl	2025, 1936, 1913		THF	2
<i>fac</i> -Mn(bpy)(CO) ₃ Br	2023, 1935, 1914		THF	3
<i>mer</i> -Mn(bpy)(CO) ₃ Br	2043, 1948, 1903		THF	3
<i>fac</i> -[Mn(bpy)(CO) ₃ (MeCN)] ⁺	2049, 1957		MeCN	4
[Mn(bpy)(CO) ₄] ⁺	2130, 2046, 2024, 1984		MeCN	4
[Mn ⁰ (mesbpy)(CO) ₃] [•]	1973, 1883, 1866		THF	5
<i>fac</i> -Mn ^I (bpy)(CO) ₃ (COOH)	2013; ~1650* and 1600*		MeCN	6
<i>fac</i> -Mn ^I (mesbpy)(CO) ₃ (COOH)	2007		THF	5
[Mn(bpy)(CO) ₂ (MeCN) ₂] ⁺	1961, 1883		MeCN	7
<i>fac</i> -Mn(bpy)(CO) ₃ H	1991, 1892, 1888		MeCN	8
[Mn(bpy)(CO) ₃] ₂	1976, 1931, 1880, 1860		2-MeTHF	9
[Mn(bpy)(CO) ₃] ₂ (μ-CN)	2152, 2043, 2035, 1946		MeCN	1
[Mn(bpy)(CO) ₃ -CN-Mn(bpy)(CO) ₃ (MeCN)] ⁺	2116, 2035, 1946, 1869	2125, ~2030, ~1940, 1870	MeCN	This work
<i>mer</i> -[Mn ^{II} (bpy)(CO) ₃ (COOH)] ⁺	2036, 1633*	2037, 2001, 1649	MeCN	This work

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