

Supporting Information for

Synthesis and Characterization of a “Turn-on” photoCORM for Trackable CO Delivery to Biological Targets

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Materials and instruments

[MnBr(CO)₅] was purchased from Strem Chemicals and was used as received. Reagents were of commercial grade and were used without further purification. All the solvents were purified according to the standard procedures.¹ 2-(pyridyl)benzthiazole (pbt) was synthesized by following a reported procedure.² A Perkin-Elmer Spectrum-One FT-IR was employed to monitor the IR spectra of the reported compounds. UV–Vis spectra were obtained with a Varian Cary 50 UV–Vis spectrophotometer. Fluorescence spectra were recorded with a Varian Cary Eclipse spectrometer. X-band EPR spectra were recorded with a Bruker EMX Spectrometer. A Zeiss AxioObserver Z1 fitted with a Hamamatsu 9100-13 EMCCD Camera was employed for the live cell imaging and the cell images were processed with the aid of iVision and ImageJ software. Horse heart myoglobin (Mb) was purchased from Aldrich and MTT was purchased from life technologies.

Synthesis of [MnBr(CO)₃(pbt)]

A batch of 100 mg (0.36 mmol) of [MnBr(CO)₅] was mixed with 76.5 mg (0.36 mmol) pbt in 20 mL of CH₂Cl₂, and the reaction mixture was stirred for 24 h at room temperature. During this time, the orange solution was covered with aluminum foil to prevent exposure from ambient light. After 24 h, the solvent was removed to obtain an orange solid, which was washed thoroughly with hexanes. Dark blocks of [MnBr(CO)₃(pbt)] in good yield (140 mg, 90%) were obtained through recrystallization by layering hexanes over its CH₂Cl₂ solution.

IR (KBr): ν_{CO} = 2030, 2022, and 1930 cm^{-1} ; UV/Vis (CH_2Cl_2), $\lambda_{\text{max}}(\epsilon)$ =315 (11000), 450 (3200); ^1H NMR data (CD_3CN): δ 9.23 (d, 1H), 8.66 (d, 1H), 8.32 (d, 1H), 8.27 (d, 1H), 8.20 (t, 1H), 7.87 (t, 1H), 7.75 (t, 2H). Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{N}_2\text{O}_3\text{SBrMn}$: C 41.75, H 1.86, N 6.49, found: C 41.67, H 1.77, N 6.52.

Crystallography

Data were collected on a Bruker APEX II single crystal X-ray diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) by ω -scan technique in the range of $3 \leq 2\theta \leq 48$ for $[\text{MnBr}(\text{CO})_3(\text{pbt})]$. The data were corrected for Lorentz polarization and absorption.³ The metal atoms are located from the Patterson maps and the rest of the non-hydrogen atoms emerged from successive Fourier syntheses. The structures were refined by full-matrix least squares procedure on F^2 . All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions. The absorption corrections are done using SADABS. Calculations were performed using SHELXTL V 6.14 program package.⁴ The Crystallographic data are presented in Table S1 and selected bond parameters are listed in Table S2.

Table S1. Crystal data and structure refinement parameters for [MnBr(CO)₃(pbt)]

Empirical formula	C15H8BrMnN2O3S
FW	431.14
Temperature (K)	296
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
<i>a</i> (Å)	15.089(3)
<i>b</i> (Å)	11.884(3)
<i>c</i> (Å)	9.095(2)
β(deg)	106.925(3)
<i>V</i> (Å ³)	1560.2(6)
<i>Z</i>	4
Density (calcd) (Mg m ³)	1.835
Abs coeff (mm ⁻¹)	3.555
No. of unique reflns	2452
^a GOF on <i>F</i> ²	1.040
^b <i>R</i> ₁	0.0584
^c <i>wR</i> ₂	0.0933

^aGOF = $[\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_v)]^{1/2}$ (*N*_o = number of observations, *N*_v = number of variables).

^b*R*₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$, ^c*wR*₂ = $[(\sum w(F_o^2 - F_c^2)^2 / \sum |F_o|^2)]^{1/2}$

Table S2. Selected bond distances (Å) and angles (°) of [MnBr(CO)₃(pbt)]

Br-Mn	2.5254(15)
Mn-C(14)	1.768(9)
Mn-C(15)	1.779(9)
Mn-C(13)	1.792(9)
Mn-N(2)	2.055(6)
Mn-N(1)	2.077(7)
C(14)-Mn-C(15)	89.7(4)
C(14)-Mn-C(13)	87.4(4)
C(15)-Mn-C(13)	86.2(4)
C(14)-Mn-N(2)	93.4(3)
C(15)-Mn-N(2)	102.5(3)
C(13)-Mn-N(2)	171.2(3)
C(14)-Mn-N(1)	94.3(3)
C(15)-Mn-N(1)	176.0(3)
C(13)-Mn-N(1)	93.5(3)
N(2)-Mn-N(1)	77.7(3)
C(14)-Mn-Br	178.2(3)
C(15)-Mn-Br	88.6(3)
C(13)-Mn-Br	93.2(3)
N(2)-Mn-Br	86.19(18)
N(1)-Mn-Br	87.38(18)

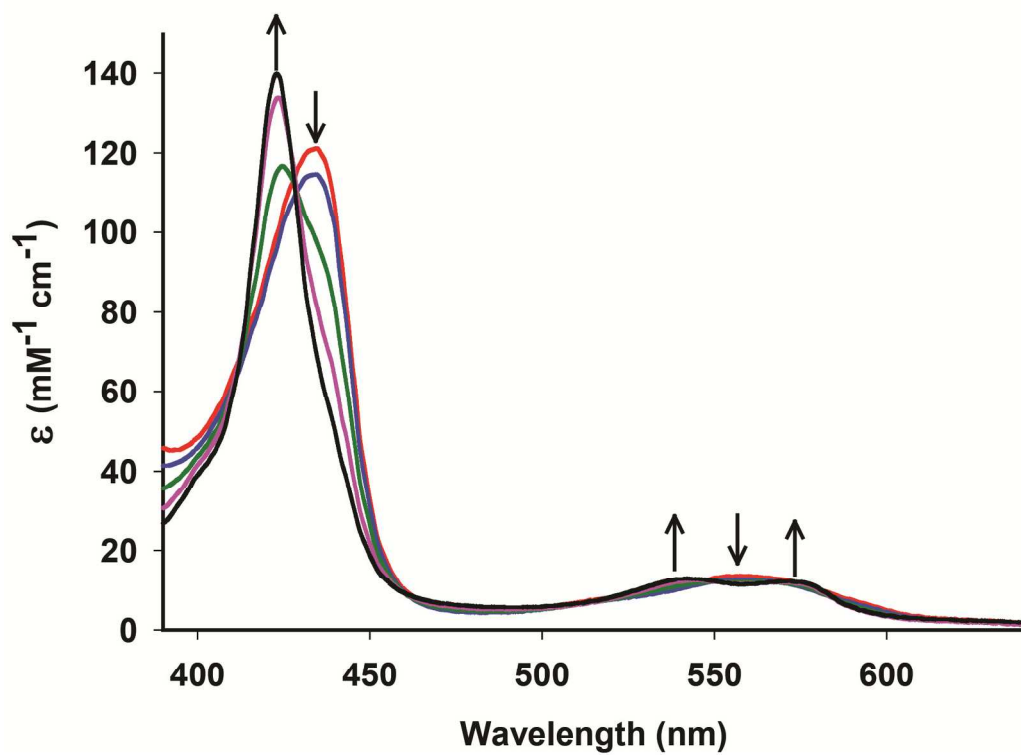


Figure S1. UV/Vis traces from the myoglobin (Mb) assay for $[\text{MnBr}(\text{CO})_3(\text{pbt})]$. Formation of the Mb-CO adduct from reduced Mb is evident by the shift in the Soret band from 435 to 424 nm.

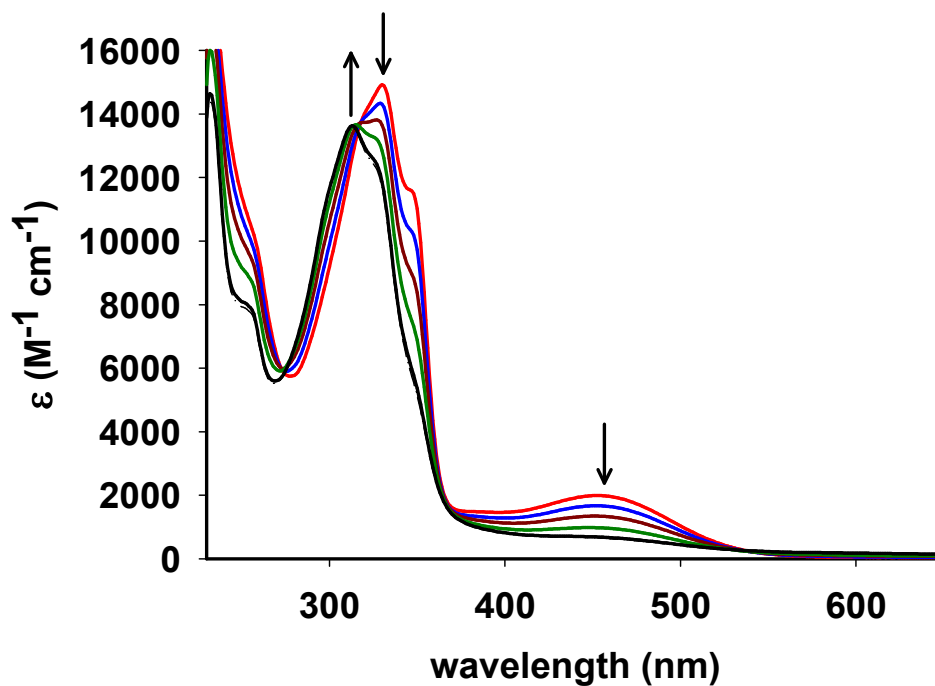


Figure S2. Changes in the electronic absorption spectrum of $[\text{MnBr}(\text{CO})_3(\text{pbt})]$ in dichloromethane solution upon exposure to the visible light (10 mW/cm^2 , without filter)

Rate = $6.48 \pm 0.01 \text{ min}^{-1}$

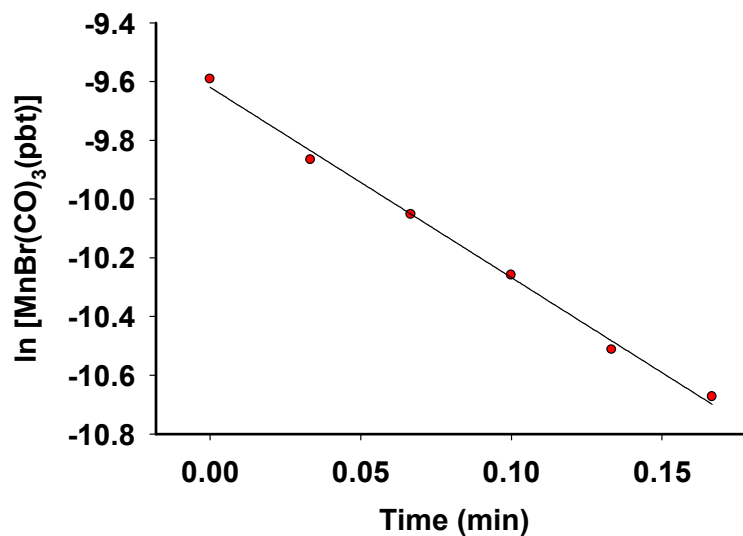


Figure S3. Plot of $\ln[\text{MnBr}(\text{CO})_3(\text{pbt})]$ vs. time (min) in dichloromethane solution at 298K upon exposure to visible light

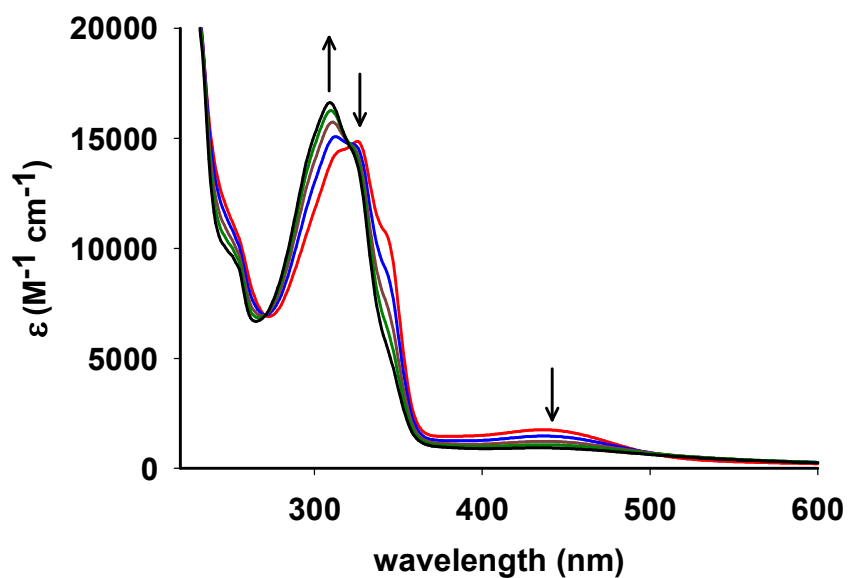


Figure S4. Changes in the electronic absorption spectrum of $[\text{MnBr}(\text{CO})_3(\text{pbt})]$ in acetonitrile solution upon exposure to the visible light ($\lambda \geq 440 \text{ nm}$, 10 mW/cm^2)

Rate = $1.05 \pm 0.01 \text{ min}^{-1}$

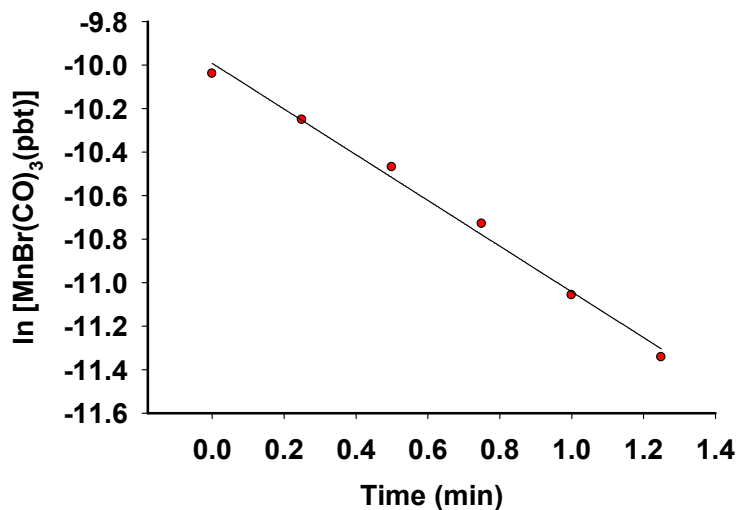


Figure S5. Plot of $\ln[\text{MnBr}(\text{CO})_3(\text{pbt})]$ vs. time (min) in acetonitrile solution at 298K upon exposure to visible light ($\lambda \geq 440 \text{ nm}$, 10 mW/cm^2)

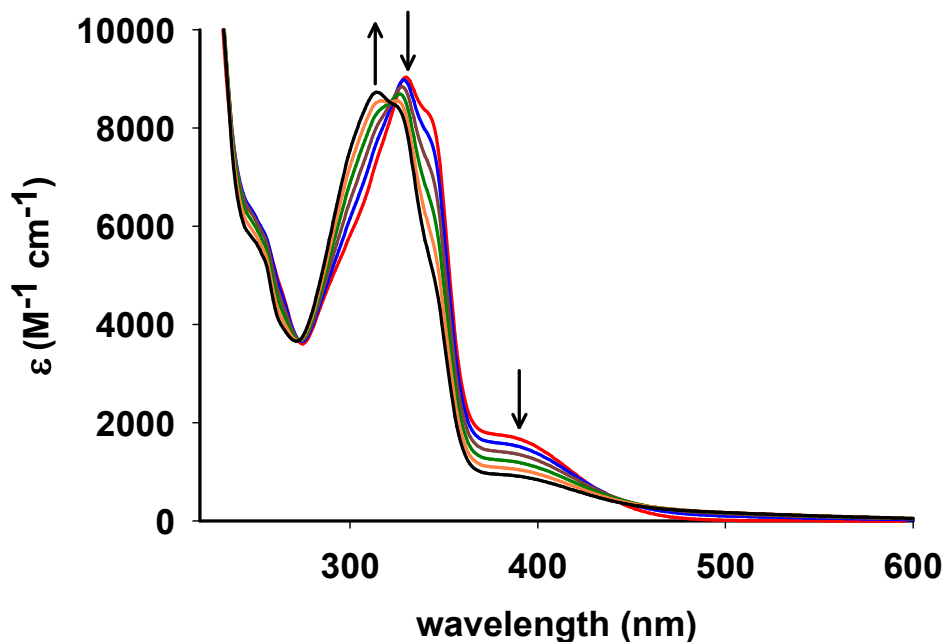


Figure S6. Changes in the electronic absorption spectrum of $[\text{MnBr}(\text{CO})_3(\text{pbt})]$ in acetonitrile-water (40:60 v/v) solution upon exposure to the visible light ($\lambda \geq 400 \text{ nm}$, 10 mW/cm^2)

Rate = $0,23 \pm 0.01 \text{ min}^{-1}$

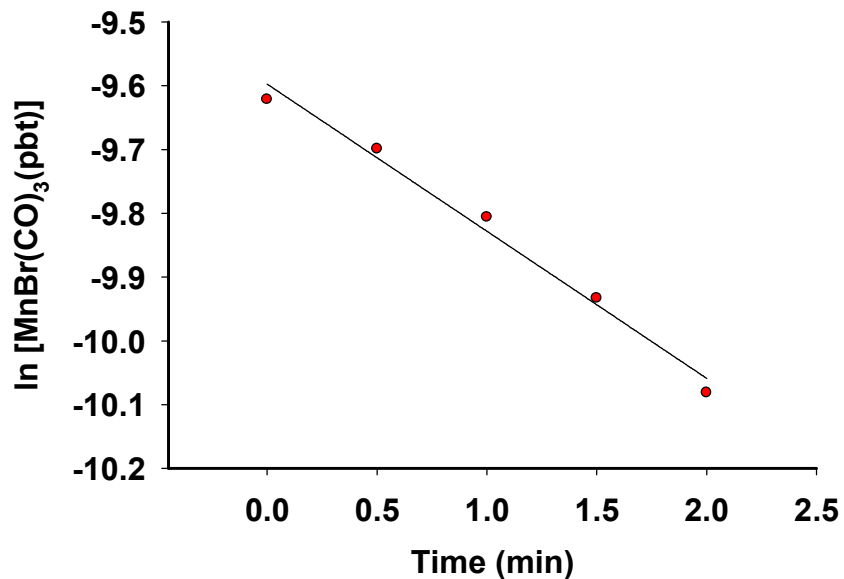


Figure S7. Plot of $\ln[\text{MnBr}(\text{CO})_3(\text{pbt})]$ vs. time (min) in acetonitrile-water (40:60 v/v) solution at 298K upon exposure to visible light ($\lambda \geq 400 \text{ nm}$, 10 mW/cm^2)

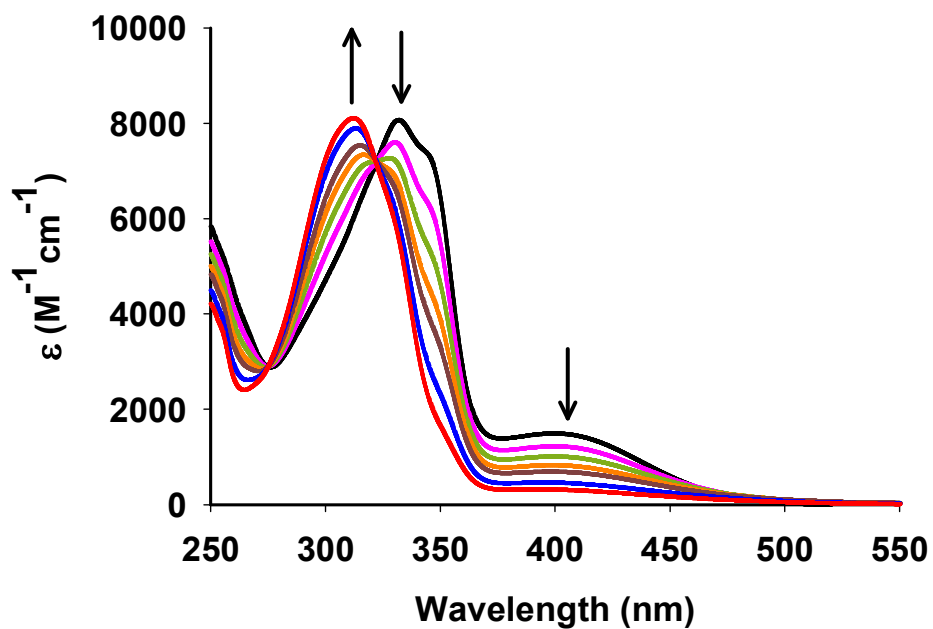


Figure S8. Changes in the electronic absorption spectrum of $[\text{MnBr}(\text{CO})_3(\text{pbt})]$ in DMSO-water (20:80 v/v) solution upon exposure to the visible light ($\lambda \geq 400 \text{ nm}$, 10 mW/cm^2)

Rate = $0.61 \pm 0.01 \text{ min}^{-1}$

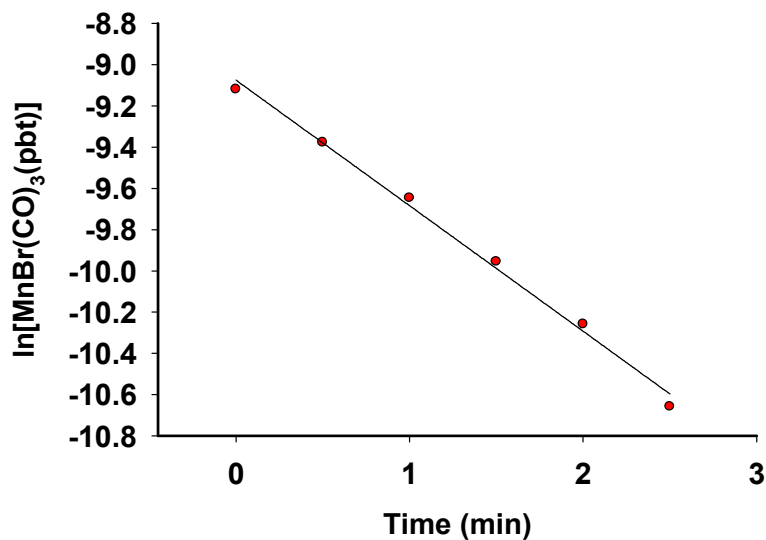


Figure S9. Plot of $\ln[\text{MnBr}(\text{CO})_3(\text{pbt})]$ vs. time (min) in DMSO-water (20:80 v/v) solution at 298K upon exposure to visible light ($\lambda \geq 400 \text{ nm}$, 10 mW/cm^2)

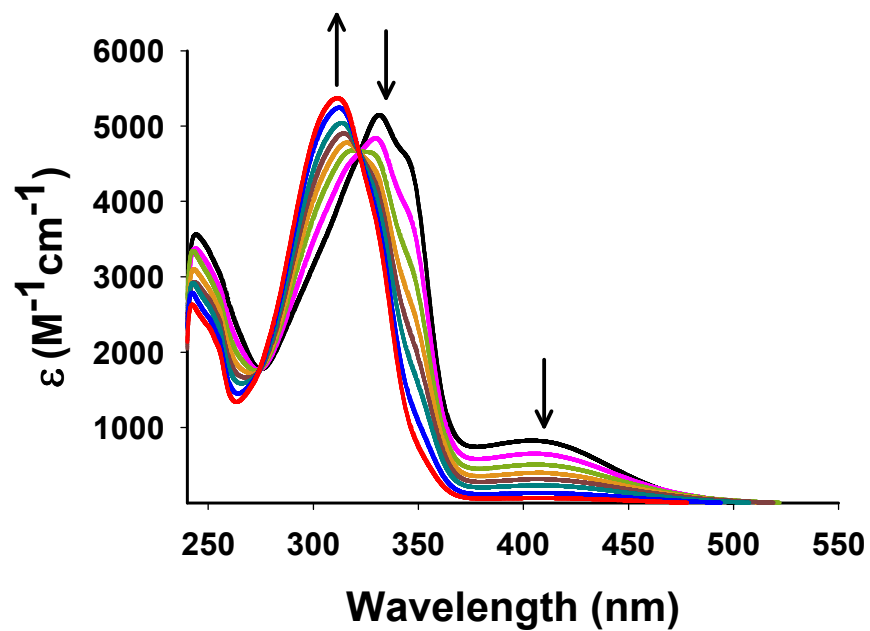


Figure S10. Changes in the electronic absorption spectrum of $[\text{MnBr}(\text{CO})_3(\text{pbt})]$ in DMSO-PBS buffer (20:80 v/v) solution upon exposure to the visible light ($\lambda \geq 400 \text{ nm}$, 10 mW/cm^2)

Rate = $0.64 \pm 0.01 \text{ min}^{-1}$

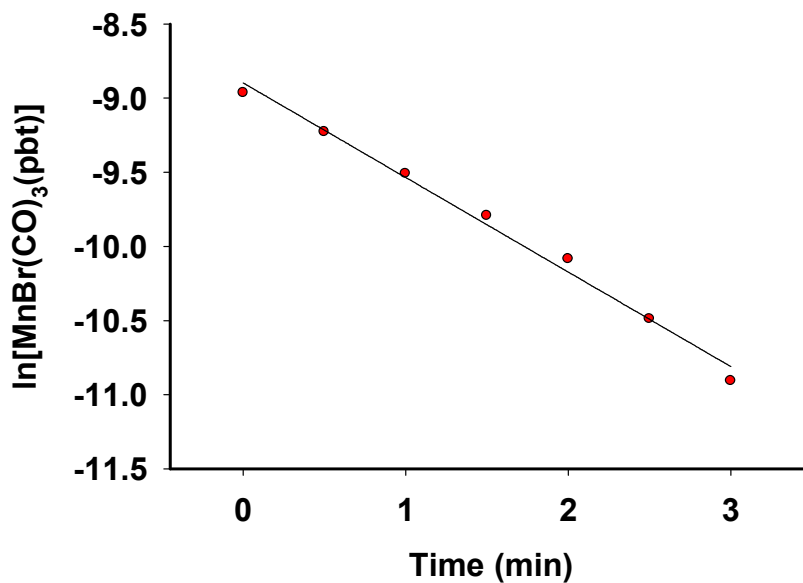


Figure S11. Plot of $\ln[\text{MnBr}(\text{CO})_3(\text{pbt})]$ vs. time (min) in DMSO-PBS buffer (20:80 v/v) solution at 298K upon exposure to visible light ($\lambda \geq 400 \text{ nm}$, 10 mW/cm^2)

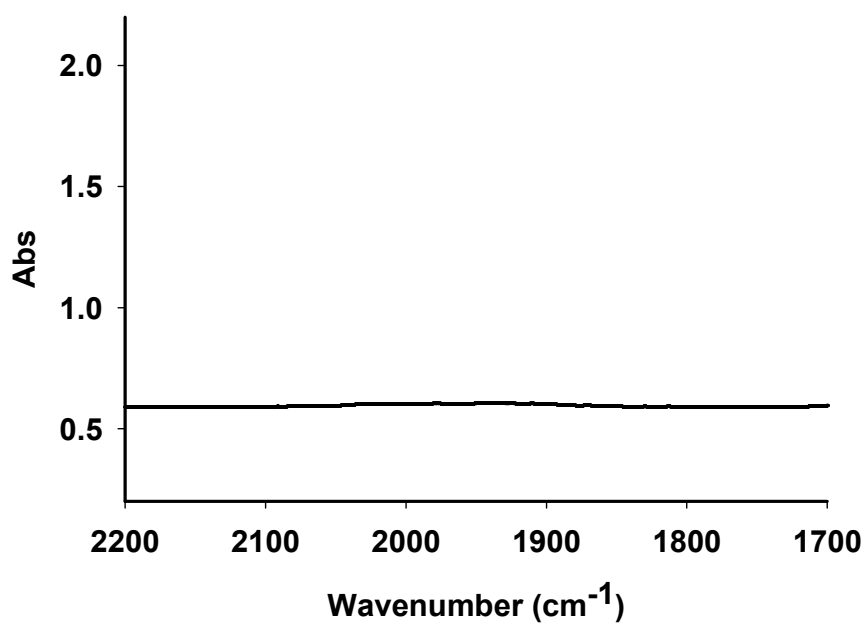
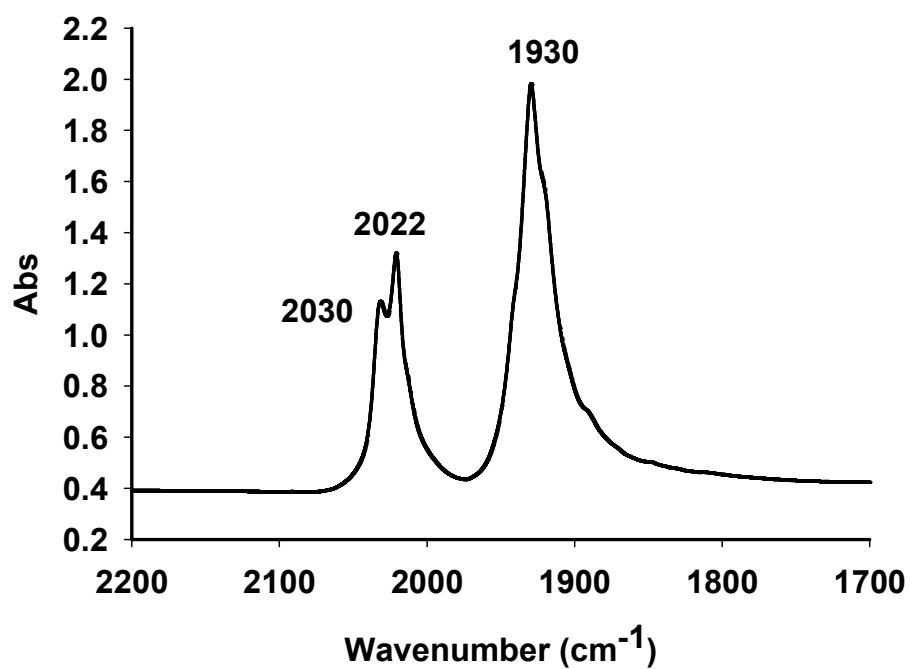


Figure S12. Solid State IR spectra (KBr disk): top figure displays the CO stretching region before photolysis of [MnBr(CO)₃(pbt)] while the bottom figure shows the same region recorded for the residue photoproduct after complete photolysis.

References

(1) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, Pergamon Press, **1988**.

(2) Gangopadhyay, J.; Sengupta, S.; Bhattacharyya, S.; Chakraborty, I.; Chakravorty, A. *Inorg. Chem.* **2002**, *41*, 2616-2622.

(3) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351-359.

(4) Sheldrick, G. M. *SHELXTL V6.14*, Bruker Analytical X-ray Systems, Madison, WI 2000.