

Supporting Information

For

**Syntheses, Structures and Properties of New Manganese Carbonyls as
Photoactive CO-releasing Molecules (photoCORMs): Design Strategies
that Lead to CO Photolability in the Visible Region**

Margarita A. Gonzalez, Samantha J. Carrington, Nicole L. Fry, Jose L. Martinez and
Pradip K. Mascharak*

Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA
95064

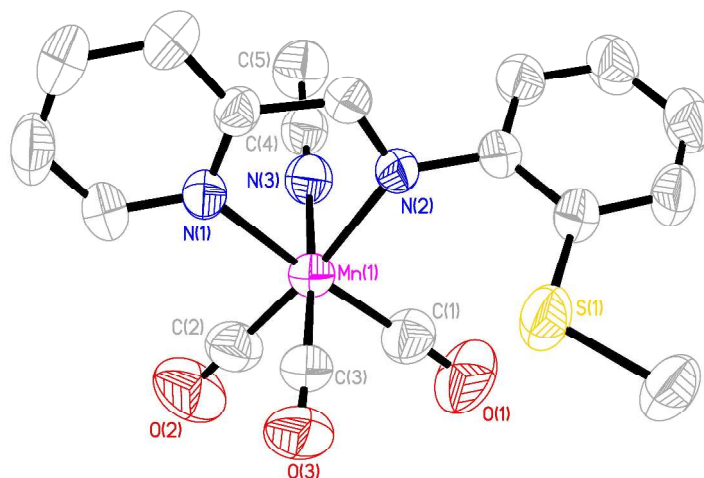


Figure S1. Thermal ellipsoid (probability level 50%) plot of $[\text{Mn}(\text{pmtpm})(\text{CO})_3(\text{MeCN})]^+$ (cation of **4**) with select atom labeling. H atoms have been omitted for clarity.

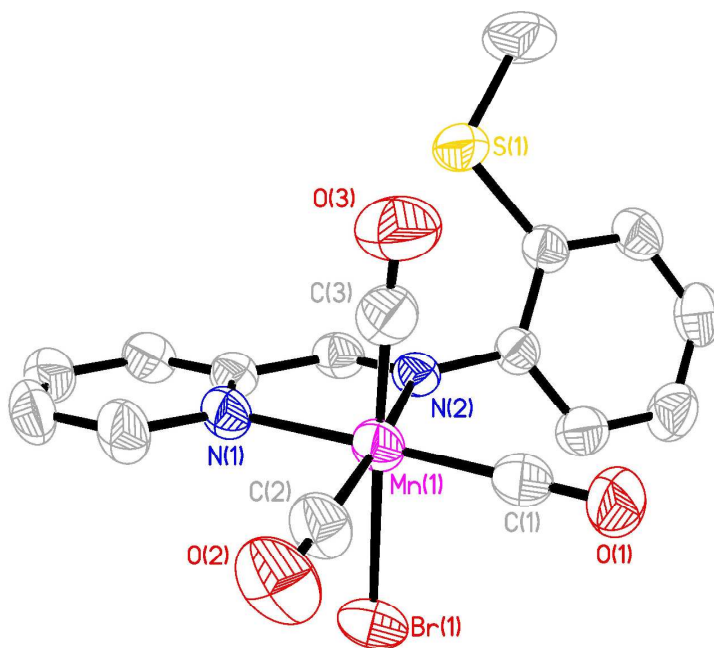


Figure S2. Thermal ellipsoid (probability level 50%) plot of $[\text{Mn}(\text{pmtpm})(\text{CO})_3\text{Br}]$ (**5**) with select atom labeling. H atoms have been omitted for clarity.

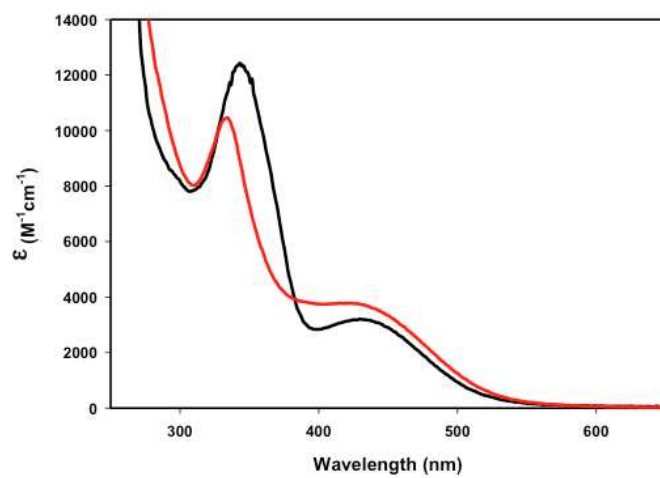


Figure S3. Electronic absorption spectra of **1** (black trace) and **2** (red trace) in MeCN

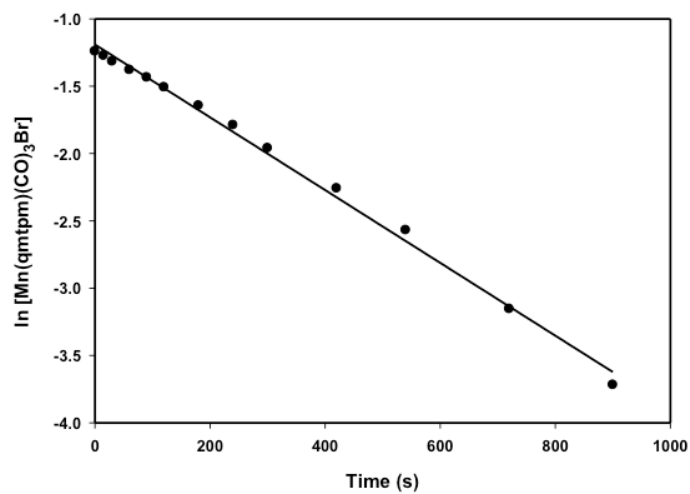


Figure S4. Plot of changes in $\ln[\mathbf{3}]$ vs. time (in s) in THF
(concentration of **3** = 1.1 mM)

Table S1. Selected Bond Distances (Å) and Angles (deg) of **1** and **4** along with the Optimized DFT Bond distances and Bond Angles for Comparison

	Complex 1		Complex 4	
	X-ray	DFT	X-ray	DFT
Mn-N1	2.126(2)	2.174	2.054(2)	2.100
Mn-N2	2.053(2)	2.085	2.069(2)	2.114
Mn-N3	2.015(2)	2.039	2.019(3)	2.047
Mn-Br	----	----	----	----
Mn-C1	1.819(3)	1.835	1.810(3)	1.844
Mn-C2	1.834(3)	1.835	1.803(3)	1.829
Mn-C3	1.801(3)	1.838	1.801(3)	1.839
C1-Mn-C2	87.02(12)	87.83	88.96(16)	90.83
C1-Mn-C3	87.56(14)	90.22	90.14(15)	91.47
C1-Mn-N2	93.94(10)	93.84	95.77(12)	94.71
C1-Mn-N3	94.28(11)	93.09	93.41(13)	92.44
C2-Mn-C3	87.51(15)	89.06	89.17(15)	90.51
C2-Mn-N1	101.03(11)	100.79	97.05(13)	96.41
C2-Mn-N3	94.80(12)	94.18	89.88(13)	89.30
C3-Mn-N1	92.61(12)	91.25	88.66(11)	88.49
C3-Mn-N2	88.50(12)	88.13	97.23(11)	96.53

Table S2: Calculated (TD-DFT) energies (E, nm), oscillator strengths (f), and nature of transitions^a in **1-5**

Energy (nm)	Oscillator Strength	Transition
Mn(pimq)(CO)₃ MeCN⁺ (1)		
431.98	0.0259762	$\pi(Q)-\pi(Ph)-\pi(MnCO) \rightarrow \pi(Q)-\pi(SB)[HOMO \rightarrow LUMO]$
406.74	0.0573702	$\pi(Q)-\pi(Ph)-d_{xz}(Mn) \rightarrow \pi(Q)-\pi(SB)[HOMO-1 \rightarrow LUMO]$
388.95	0.0307494	$\pi(MnCO)-\pi(Ph) \rightarrow \pi(Q)-\pi(SB)[HOMO-2 \rightarrow LUMO]$
379.85	0.0170396	$\pi(MnCO)-\pi(Ph) \rightarrow \pi^*(CO)-d_{yz}(Mn)[HOMO-2/HOMO-3 \rightarrow LUMO+2]$
369.81	0.0218921	$\pi(MnCO)-\pi(Ph)-\pi(Q) \rightarrow \pi^*(CO)-d_{yz}(Mn)[HOMO-5 \rightarrow LUMO+2]$
366.02	0.0471654	$\pi(MnCO)-\pi(Ph)-\pi(Q) \rightarrow \pi(Q)-\pi(SB)[HOMO-5 \rightarrow LUMO]$
364.38	0.1583092	$\pi(MnCO)-\pi(Ph) \rightarrow \pi(Q)-\pi(SB)[HOMO-4/HOMO-5 \rightarrow LUMO]$
356.96	0.0065401	$\pi(Q)-\pi(Ph)-\pi(MnCO) \rightarrow \pi^*(CO)-d_{yz}(Mn)[HOMO \rightarrow LUMO+2]$
348.25	0.0057679	$\pi(Ph)-d_{yz}(Mn) \rightarrow \pi(Q)-\pi(SB)[HOMO-4 \rightarrow LUMO]$
311.86	0.0044184	$\pi(MnCO)-\pi(Ph)-\pi(Q) \rightarrow \pi^*(CO)-d_{xz}(Mn)[HOMO-5 \rightarrow LUMO+3]$
308.04	0.0599235	$\pi(Q)-\pi(Ph) \rightarrow \pi(Q)-\pi(SB)[HOMO-6 \rightarrow LUMO]$
Mn(qmtpm)(CO)₃ MeCN⁺ (2)		
533.21	0.0450962	$\pi(PhS) \rightarrow \pi(Q)-\pi(SB)[HOMO \rightarrow LUMO]$
459.29	0.0122483	$\pi(MnCO)-\pi(Q) \rightarrow \pi(Q)-\pi(SB)[HOMO-1 \rightarrow LUMO]$
432.41	0.0189162	$\pi(MnCO)-\pi(Q) \rightarrow \pi(Q)-\pi(SB)[HOMO-2/HOMO-3 \rightarrow LUMO]$
417.86	0.0334093	$\pi(MnCO)-\pi(Q) \rightarrow \pi(Q)-\pi(SB)[HOMO-2 \rightarrow LUMO]$
374.61	0.0121610	$\pi(Q)-\pi(PhS)-\pi(MnCO) \rightarrow \pi(Q)-\pi(SB)[HOMO-4 \rightarrow LUMO]$
367.31	0.1417877	$\pi(PhS)-\pi(Q)-d_{yz}(Mn) \rightarrow \pi(Q)-\pi(SB)[HOMO-5 \rightarrow LUMO]$
317.04	0.0064779	$\pi(PhS) \rightarrow \pi(Q)-\pi(SB)[HOMO \rightarrow LUMO+1]$
312.28	0.0633768	$\pi(Q)-\pi(PhS) \rightarrow \pi(Q)-\pi(SB)[HOMO-6 \rightarrow LUMO]$
311.55	0.0258245	$\pi(Q)-\pi(PhS) \rightarrow \pi(Q)-\pi(SB)[HOMO-6 \rightarrow LUMO]$
Mn(qmtpm)(CO)₃ Br (3)		
520.47	0.0046467	$\pi(PhS) \rightarrow \pi(Q)-\pi(SB)[HOMO \rightarrow LUMO]$
484.31	0.0166749	$p(Br)-\pi(MnCO) \rightarrow \pi(Q)-\pi(SB)[HOMO-1 \rightarrow LUMO]$
460.92	0.0533586	$p(Br)-\pi(MnCO) \rightarrow \pi(Q)-\pi(SB)[HOMO-2 \rightarrow LUMO]$
386.85	0.0261170	$p(Br)-\pi(MnCO) \rightarrow \pi^*(CO)-d_{xz}(Mn)[HOMO-2 \rightarrow LUMO+2]$
385.60	0.0560467	$p(Br)-\pi(MnCO)-\pi(PhS)-\pi(Q) \rightarrow \pi(Q)-\pi(SB)[HOMO-5 \rightarrow LUMO]$
380.86	0.0221435	$\pi(Q)-p(Br) \rightarrow \pi(Q)-\pi(SB)[HOMO-4 \rightarrow LUMO]$
355.68	0.0707132	$\pi(PhS)-\pi(MnCO)-p(Br) \rightarrow \pi(Q)-\pi(SB)[HOMO-6 \rightarrow LUMO]$
310.29	0.0543400	$p(Br)-\pi(MnCO) \rightarrow \pi(Q)-\pi(SB)[HOMO-1 \rightarrow LUMO+1]$
305.82	0.0213883	$p(Br)-\pi(MnCO) \rightarrow \pi(Q)-\pi(SB)[HOMO-1 \rightarrow LUMO+1]$
301.94	0.0172565	$p(Br)-\pi(MnCO) \rightarrow \pi^*(CO)-d_{xz}(Mn)[HOMO-1 \rightarrow LUMO+4]$
Mn(pmtpm)(CO)₃ MeCN⁺ (4)		
484.60	0.0301023	$\pi(PhS) \rightarrow \pi(Pyr)-\pi(SB)[HOMO \rightarrow LUMO]$
381.93	0.0079797	$\pi(MnCO)-\pi(PhS) \rightarrow \pi(Pyr)-\pi(SB)[HOMO-3 \rightarrow LUMO]$
372.72	0.0491039	$\pi(MnCO) \rightarrow \pi(Pyr)-\pi(SB)[HOMO-2 \rightarrow LUMO]$
369.87	0.0041212	$\pi(MnCO) \rightarrow \pi^*(CO)-d_{x^2-y^2}(Mn)[HOMO-2 \rightarrow LUMO+2]$

362.67	0.0065383	$\pi(\text{MnCO})-\pi(\text{PhS})\rightarrow\pi^*(\text{CO})-\text{d}_{x^2-y^2}(\text{Mn})[\text{HOMO-4}\rightarrow\text{LUMO}+2]$
355.35	0.0066387	$\pi(\text{MnCO})-\pi(\text{PhS})\rightarrow\pi^*(\text{CO})-\text{d}_{x^2-y^2}(\text{Mn})[\text{HOMO-1}\rightarrow\text{LUMO}+2]$
346.30	0.0606618	$\pi(\text{MnCO})-\pi(\text{PhS})\rightarrow\pi(\text{Pyr})-\pi(\text{SB})[\text{HOMO-4}\rightarrow\text{LUMO}]$
340.15	0.0041995	$\pi(\text{MnCO})-\pi(\text{PhS})\rightarrow\pi^*(\text{CO})-\text{d}_{x^2-y^2}(\text{Mn})[\text{HOMO-1}\rightarrow\text{LUMO}+2]$
317.56	0.0043599	$\pi(\text{MnCO})\rightarrow\pi^*(\text{CO})-\text{d}_{x^2-y^2}(\text{Mn})[\text{HOMO-2}\rightarrow\text{LUMO}+3]$
310.03	0.0106036	$\pi(\text{PhS})\rightarrow\pi(\text{Pyr})-\pi(\text{SB})[\text{HOMO}\rightarrow\text{LUMO}+1]$
306.70	0.0051657	$\pi(\text{PhS})\rightarrow\pi(\text{Pyr})-\pi(\text{SB})[\text{HOMO}\rightarrow\text{LUMO}+1]$
300.95	0.0167035	$\pi(\text{PhS})\rightarrow\pi^*(\text{CO})-\text{d}_{x^2-y^2}(\text{Mn})[\text{HOMO}\rightarrow\text{LUMO}+2]$

Mn(pmtpm)(CO)₃ Br (5)

491.25	0.0061503	$\pi(\text{PhS})\rightarrow\pi(\text{Pyr})-\pi(\text{SB})[\text{HOMO}\rightarrow\text{LUMO}]$
446.20	0.0241548	$\pi(\text{MnCO})-\text{p}(\text{Br})\rightarrow\pi(\text{Pyr})-\pi(\text{SB})[\text{HOMO-2}\rightarrow\text{LUMO}]$
377.25	0.0088643	$\pi(\text{MnCO})-\text{p}(\text{Br})\rightarrow\pi^*(\text{CO})-\text{d}_{xz}(\text{Mn})[\text{HOMO-2}\rightarrow\text{LUMO}+2]$
354.91	0.0078422	$\pi(\text{MnCO})-\text{p}(\text{Br})\rightarrow\pi^*(\text{CO})-\text{d}_{yz}(\text{Mn})[\text{HOMO-1}\rightarrow\text{LUMO}+3]$
348.05	0.0197345	$\pi(\text{PhS})-\pi(\text{MnCO})-\text{p}(\text{Br})\rightarrow\pi(\text{Pyr})-\pi(\text{SB})[\text{HOMO-5}\rightarrow\text{LUMO}]$
343.00	0.0659919	$\pi(\text{PhS})-\text{p}(\text{Br})-\pi(\text{MnCO})\rightarrow\pi(\text{Pyr})-\pi(\text{SB})[\text{HOMO-4}\rightarrow\text{LUMO}]$

^a Orbitals with greater contributions listed first