Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

For

Exceptionally rapid CO release from a Manganese(I) tricarbonyl complex derived from bis(4-chloro-phenylimino)acenaphthene upon exposure to visible light

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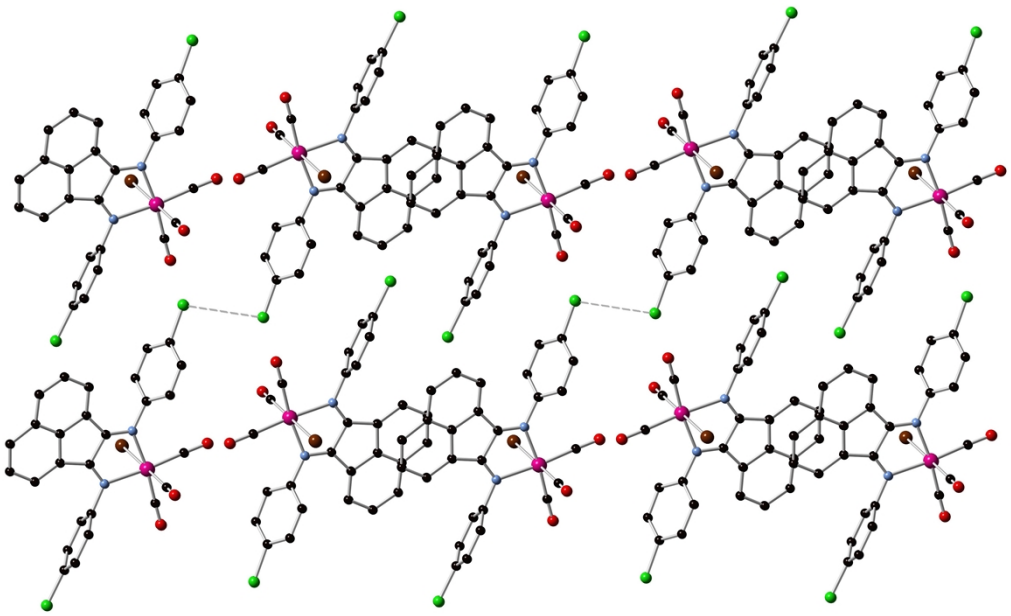

Figure S1. Packing diagram of **1** showing growth along the y axis. The intermolecular Cl–Cl interactions (3.565 Å) are shown in addition to π-stacking (centroid to centroid distance 3.707 Å).

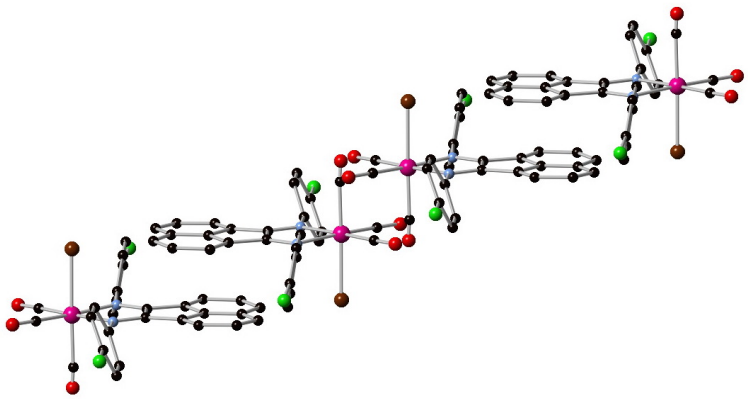

Figure S2. Packing diagram of **1** showing growth along the x axis. The π-stacking is highlighted.

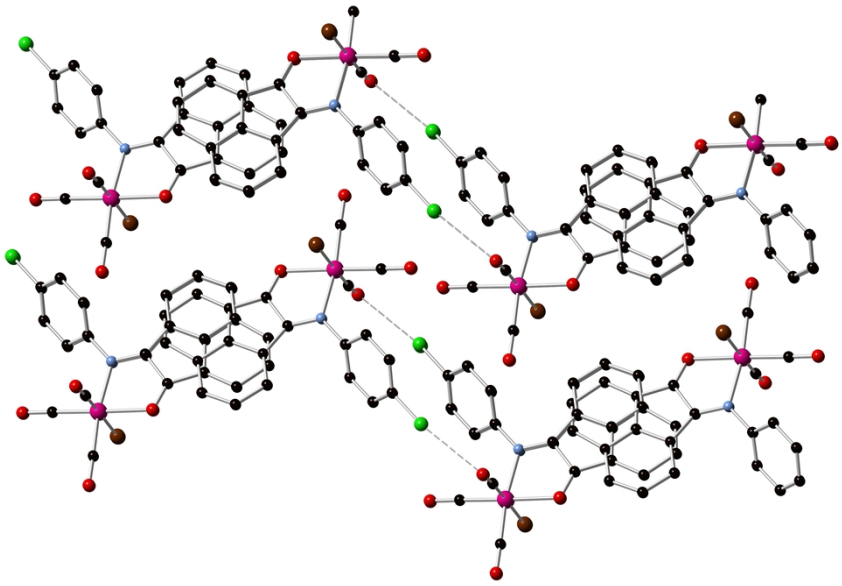

Figure S3. Packing diagram of **2** showing growth along the x axis. The Cl–O interactions (3.213 Å) are shown in addition to π-stacking (centroid to centroid distance 3.681 Å).

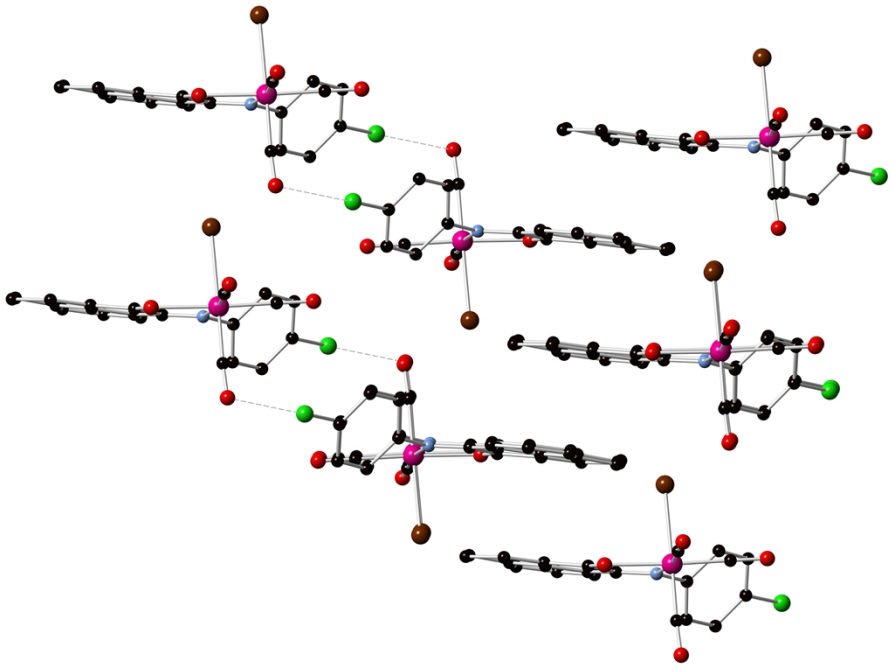

Figure S4. Packing diagram of **2** showing growth along the y axis. The Cl–O interactions are shown in addition to π–stacking.

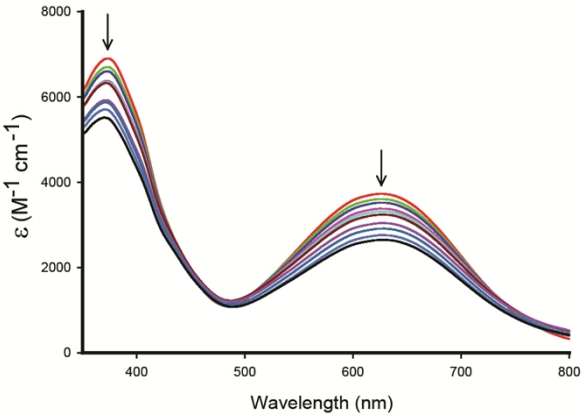

Figure S5. Spectral traces of **2** in CH_2Cl_2 298 K with low power visible light (15 mW/cm^2)

Table S1. Selected Bond distances (Å) and angles (º) of **1** and **2** along with Optimized DFT Bond Distances and Bond Angles for Comparison.

	1		**2**	
	X-ray	**DFT**	**X-ray**	**DFT**
Mn(1)-C(1)	1.963(15)	1.773	1.819(11)	1.782
Mn(1)-C(2)	1.808(8)	1.806	1.776(13)	1.810
Mn(1)-C(3)	1.810(8)	1.806	1.797(11)	1.786
Mn(1)-N(1)	2.063(6)	2.043	2.057(7)	2.029
Mn(1)-N(2)	2.056(6)	2.033	–	–
Mn(1)-O(4)	–	–	2.096(8)	2.092
Mn(1)-Br(1)	2.4900(14)	2.527	2.509(4)	2.509
C(2)-Mn(1)-C(3)	90.0(4)	90.7	88.2(5)	89.8
C(2)-Mn(1)-C(1)	89.3(6)	92.7	89.0(5)	91.9
C(3)-Mn(1)-C(1)	90.0(5)	92.7	90.4(4)	91.2
C(2)-Mn(1)-N(2)	95.8(3)	94.9	–	–
C(3)-Mn(1)-N(2)	173.1(3)	172.3	–	–
C(1)-Mn(1)-N(2)	94.0(5)	92.3	–	–
C(2)-Mn(1)-N(1)	174.9(3)	171.7	171.8(4)	169.5
C(3)-Mn(1)-N(1)	95.2(3)	94.6	98.5(4)	97.7
C(1)-Mn(1)-N(1)	91.0(5)	93.4	95.5(4)	95.2
N(2)-Mn(1)-N(1)	79.1(2)	79.2	–	–
C(2)-Mn(1)-O(4)	–	–	94.4(5)	92.3
C(3)-Mn(1)-O(4)	–	–	176.0(4)	174.9
C(1)-Mn(1)-O(4)	–	–	92.7(4)	93.4
N(1)-Mn(1)-O(4)	–	–	78.7(3)	79.7
C(2)-Mn(1)-Br(1)	90.7(2)	87.3	88.3(4)	86.0
C(3)-Mn(1)-Br(1)	89.3(3)	87.0	90.9(3)	88.4
C(1)-Mn(1)-Br(1)	179.3(5)	179.7	177.1(3)	177.9
N(2)-Mn(1)-Br(1)	86.74(16)	88.0	–	–
N(1)-Mn(1)-Br(1)	89.11(15)	86.6	87.0(2)	86.9
O(4)-Mn(1)-Br(1)	–	–	86.2(2)	87.1

Table S2. Calculated (TD-DFT) energies (E, nm), oscillation strengths (f), and nature of transitions[a] for complexes **1** and **2.**

1

Energy (nm)	*f*	Transition
585	0.0217148	π(Mn-CO), p–(Br^-), π (phenyl)→ π*(imine-phenyl-acenaphthene)[HOMO →LUMO]
401	0.1247711	π (Mn-CO), p(Br^-), π (phenyl)→ π*(imine-phenyl-acenaphthene)[HOMO-4 →LUMO]
393	0.0338000	π (phenyl)→ π*(imine-phenyl-acenaphthene)[HOMO-5 →LUMO]
380	0.0531048	π (phenyl), π (Mn-CO)→ π*(imine-phenyl-acenaphthene)[HOMO-6 →LUMO]
336	0.2156214	π (Mn-CO), π (acenaphthene), π (phenyl)→ π*(acenaphthene), π*(imine) π*(phenyl)[HOMO-3 →LUMO+1]
331	0.0476880	π (Mn-CO), p (Br^-), π (phenyl)→ π*(imine-phenyl-acenaphthene)[HOMO-8 →LUMO]

2

Energy (nm)	*f*	Transition
660	0.0302665	π (Mn-CO), p–(Br^-) → π*(imine-acenaphthene), π*(phenyl)[HOMO-1→LUMO]
437	0.1223185	π (Mn-CO), π(acenaphthene), p–(Br^-)→π*(imine-acenaphthene), π*(phenyl)[HOMO-4 →LUMO]
411	0.0700559	π (phenyl), π (Mn-CO)→ π*(imine-acenaphthene), π*(phenyl)[HOMO-5 →LUMO]
378	0.0249890	π (phenyl), π(Mn-CO)→ π*(imine-acenaphthene), π*(phenyl) [HOMO-6 →LUMO]
335	0.0365679	π (Mn-CO), π (acenaphthene), p–(Br^-)→π*(acenaphthene), π*(imine) π*(phenyl) [HOMO-4 →LUMO+1]

[a]Orbitals with greater contributions listed first