

Supporting information

**A comprehensive survey of the Mn(I) carbonyls as CO-releasing molecules
over the last two decades**

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Table 1 The CO releasing kinetics of Mn(I) carbon monoxide releasing properties								
CORM	Activation method	CO release Monitoring	CO equivalents (Or moles)	$t_{1/2}$ (min or s)	Solvent used	k_{CO} (min^{-1} or s^{-1})	Quantum yield (Φ_{CO})	Ref
3.1.1. Monodentate ancillary ligands								
CORM-1 ^a	Cold light	¹ Mb			DMSO			23
1a and 1b ^b	365 nm	Mb	1a: 2.2 ± 0.1 equiv. 1b: 2.6 ± 0.4 equiv.	1a: 6.4 ± 0.1 min 1b: 5.6 min	Aqueous media			44
2	468 nm	Mb		21.21 min	DMSO	$5.05 \times 10^{-4} \text{ s}^{-1}$		45
3a–3f	350 nm	Mb	2 ± 0.33 equiv.		DCM (< 5 %)			46
3.1.2. <i>N,N</i> -bidentate ligands								
3.1.2.1. 2,2'-Bipyridine photoCORMs								
4–6	510 nm	Mb		4a: 693 s 4b: 1733 s 5: 288 s 6: 1066 s	THF			47, 48
7 ^c	Green, blue, and UV light	Mb/CO detector	2.2 moles	Green: 13 min Blue: 4 min UV: 1 min	PBS	Mb (min^{-1}): Green: 0.053, Blue: 0.173, and UV: 0.693. CO detector ($\text{g}/(\text{mol}\cdot\text{min})$) Green: 15.15, Blue: 30.49, and UV: 38.42		48
4a, 8a and 8b	405 or 470 nm	¹ FTIR and ¹ H NMR spectroscopy			CH ₃ CN		4a: 0.22 ± 0.01 8a: 0.20 ± 0.01 8b: 0.32 ± 0.02	50
9a–9c	405 or 470 nm	FTIR and ¹ H NMR spectroscopy			CH ₃ CN		9a: 0.17 ± 0.01 9b: 0.15 ± 0.01 9c: 0.19 ± 0.01	50, 51
10a and 10b	405 nm	FTIR, UV-vis, and ¹ H NMR spectroscopy			CH ₃ CN		10a: 0.38 ± 0.01 10b: 0.27 ± 0.01	50
4a, 11a–11c	420 (4, 11a), 470 (11b), 510 (11c) nm	Ultrafast ¹ TA spectroscopy			CH ₃ CN (4a, 11a–11c) and CHCl ₃ (4a)			52
12a–12d	365 nm	Mb	12a: 1.66 equiv. 12b: 2.05 equiv. 12c: 2.18 equiv. 12d: 2.22 equiv.	12a: 8.41 min 12b: 5.04 min 12c: 8.86 min 12d: 10.70 min	DMSO			54
13a, 13b, 14, 15a, and 15b	365 nm	Mb	13a: 2.4 equiv. 13b: 1.0 equiv. 14: 2.1 equiv. 15a: 1.4 equiv.	13a: 5.7 min 13b: 6.4 min 14: 4.8 min 15a: 9.5 min	DMSO			55

			15b : 2.0 equiv.	15b : 6.9 min				
16a–16e	365 nm	Mb	16a : 1.4 equiv. 16b : 1.4 equiv. 16c : 1.5 equiv. 16d : 1.7 equiv. 16e : 2.2 equiv.	16a : 9.5 min 16b : 11.4 min 16c : 13.9 min 16d : 3.9 min 16e : 8.7 min	DMSO			56
17a and 17b^d	365 nm	Mb	17a : 2.01 equiv. 17b : 1.31 equiv.	17a : 12.41 min 17b : 14.05 min	DMSO			57
3.1.2.2. 1,10-phenanthroline photoCORMs								
4, 18–20	UV light and low power (15 mW/cm ²) visible light	UV-vis, and Mb.			DCM	4 : Vis: 1.21 ± 0.02 UV: 12.11 ± 0.0 18 : Vis: 4.65 ± 0.03 UV: 2.44 ± 0.03 19 : Vis: 3.44 ± 0.02 UV: 3.18 ± 0.02 20 : Vis: 6.29 ± 0.03 UV: 0.94 ± 0.03		58
21	Low power (15 mW/cm ²) visible light (> 405 nm)	FTIR and Mb.	3 CO were released		CH ₃ CN	10.5 ± 0.02	0.35 ± 0.03	59
22	Low power (15 mW/cm ²) visible light	FTIR and Mb.	3 CO were released		CH ₃ CN, and 2% (v/v) CH ₃ CN/PBS	0.13	0.39 ± 0.03	60
23 and 24	365–555 nm	FTIR and ¹ H NMR spectroscopy			Acetone DCM			61
25	Low power (10 mW/cm ²) visible light	Mb			PBS	0.0030 ± 0.010 (s ⁻¹)		62
26	420 nm	Mb	26 : 2.3 ± 0.02	26 : 3.31 ± 2.30	PBS			63
27a	350 nm	Mb, ⁵ EPR, FTIR, and NMR spectroscopy			CH ₃ CN, DCM, CH ₃ CN/H ₂ O, and H ₂ O			65
27b	Low power (15 mW/cm ²) visible light	Mb, EPR, and FTIR spectroscopy			CH ₃ CN, DMSO and PBS	PBS: 0.44 ± 0.02 CH ₃ CN: 0.51 ± 0.02		66
28–30	435–450 nm	Mb	1.4 equiv.	28 : 23 min 29a : 13 min 29b : 10 min 30 : 6 min	DCM and 0.5% (v/v) DMSO/H ₂ O			67

31	730 nm	Mb, EPR, and FTIR spectroscopy			CHCl ₃ and CH ₃ CN	31 : 0.0566 ± 0.0008 min ⁻¹	31 : 0.064 ± 0.002	68
3.1.2.3. κ²N¹N²- terpyridine photoCORMs								
32a–32h	372 nm	FTIR and ¹ H NMR spectroscopy			CH ₃ CN		32e : 0.7	70 , 71
33a–33h	372 nm	FTIR and ¹ H NMR spectroscopy			CH ₃ CN and H ₂ O			71
34 and 35	405 and 451 nm 750 and 800 nm lasers	¹³ C–TCD	35 : 2.53 ± 0.06 (After 180 min of illumination at 451 nm in aerobic EtOH)		H ₂ O, EtOH, EtOH/H ₂ O, and EtOH/PBS		35 at 451 nm Aerobic EtOH: 0.258–0.277 Anaerobic EtOH: 0.233–0.252	72
36	410 nm	Mb		9.8 min ^a	CH ₃ CN	0.07065		73
37–42	- 468 nm - 525 nm	Mb	At 468 nm: 37 : 3.00 ± 0.03 equiv. 39 : 5.66 ± 0.16 equiv. ^f 41 : 2.64 ± 0.03 equiv.	37 : 1.52 ± 0.03 min 39 : 1.68 ± 0.04 min 41 : 2.22 ± 0.15 min	DMSO	37 : (0.76 ± 0.01) × 10 ⁻² s ⁻¹ 39 : (7.0 ± 0.05) × 10 ⁻² s ⁻¹ 41 : (5.0 ± 0.03) × 10 ⁻² s ⁻¹		74
3.1.2.4. Benzimidazole and benzothiazole photoCORMs								
43a and 43b, 44	468 nm	Mb and ¹ H NMR spectroscopy		43a : 7.82 min 43b : 2.53 min 44 : 11.42 min	DMSO	43a : 0.0014 s ⁻¹ 43b : 0.0045 s ⁻¹ 44 : 0.0010 s ⁻¹		75
45 and 46	468 nm	Mb	2.5 equiv.	45 : 7.2 min 46 : 2.59 min	DMSO	45 : 0.0016 s ⁻¹ 46 : 0.0037 s ⁻¹		76
47, 48, 49a, 49b, 50	468 nm	Mb	47 and 48 : 2 equiv. 49 and 50 : 5 equiv.	47 : 3.28 48 : 3.05 49a : 2.04 49b : 10.07 50 : 3.75	DMSO	47 : 35.3 × 10 ⁻⁴ s ⁻¹ 48 : 38.1 × 10 ⁻⁴ s ⁻¹ 49a : 56.9 × 10 ⁻⁴ s ⁻¹ 49b : 11.5 × 10 ⁻⁴ s ⁻¹ 50 : 30.8 × 10 ⁻⁴ s ⁻¹		77
43a⁷⁵, 44⁷⁷, 51⁷⁸ and 52⁷⁸	365 nm	Mb, CO sensor, and FTIR spectroscopy		43a : 15 min 44 : 5 min 51 : 6 min 52 : 10 min	DMSO and CH ₃ CN	43a : 1.9 44 : 10.8 51 : 8.0 52 : 3.4	43a : 0.12 44 : 0.36 51 : 0.28 52 : 0.16	75 , 77 , 78
53a–53h	412–525 nm	CO sensor, and FTIR spectroscopy	468 nm: 0.9–1.8 equiv. 525 nm: 53f : 0.9 equiv.		DMSO and 10 % (v/v) DMSO/H ₂ O			79
54	400–440 nm	Mb			DCM CH ₃ CN 40% (v/v) CH ₃ CN/H ₂ O O	4.32 ± 0.01 (DCM) 1.05 ± 0.01 (CH ₃ CN) 0.23 ± 0.01 (40% (v/v) CH ₃ CN/H ₂ O)		80

					20% (v/v) DMSO/H ₂ O	0.61 ± 0.01 (20% (v/v) DMSO/H ₂ O)		
55 and 56	Low power (10 mW/cm ²) visible light	Mb			CH ₃ CN	55: 0.98 ± 0.02 56: 2.51 ± 0.02		81
57	Low power (15 mW/cm ²) visible light	Mb, EPR, and FTIR spectroscopy			CH ₃ CN DMSO PBS	PBS: 1.54 ± 0.02 CH ₃ CN: 0.91 ± 0.02		66
58 and 59	low-power (mW levels) broadband visible light	Mb			DCM	58: 0.96 min ⁻¹		82
3.1.2.5. N,N-Schiff-base PhotoCORMs								
60a, 60b, 61a, 61b, 62a, 62b	400–550 nm	Mb			CH ₃ CN THF	60: (2.1 ± 0.1) × 10 ⁻³ s ⁻¹ 60b: (1.1 ± 0.1) × 10 ⁻³ s ⁻¹ 61a: (2.6 ± 0.1) × 10 ⁻³ s ⁻¹ 61b: (2.0 ± 0.1) × 10 ⁻³ s ⁻¹ 62b: (1.4 ± 0.1) × 10 ⁻³ s ⁻¹	60a: 0.340 ± 0.010 60b: 0.116 ± 0.010 61a: 0.370 ± 0.010 61b: 0.208 ± 0.010 62b: 0.130 ± 0.010	83
63 and 64	≥ 520 nm	Mb, and FTIR spectroscopy			DMSO 10% (v/v) DMSO/H ₂ O CH ₂ Cl ₂ CH ₃ CN	63: 25.9 ± 0.2 ^f 64: 11.1 ± 0.2	63: 15.2 s	84
65–67	Low power (10–15 mW/cm ²) visible light	Mb, and EPR, spectroscopy			DMSO, DCM and PBS	65: 5.56 ± 0.02 ⁿ 66: 12.43 ± 0.02 67: 2.84 ± 0.02		85
68	468 nm 525 nm		525 nm: one equiv. 468 nm: three equiv.	525 nm: 27.85 ± 1.60 min 468 nm: 2.01 ± 0.21 min	DMSO	525 nm: (0.40 ± 0.03) × 10 ⁻³ s ⁻¹ 468 nm: (0.59 ± 0.03) × 10 ⁻² s ⁻¹		86
69 and 70	Broad band (15 mW/cm ²) visible light	Mb			2% (v/v) CH ₃ CN/PB S CH ₃ CN DCM CHCl ₃	69: 1.03 70: 0.66	69: 0.35 ± 0.02 70: 0.23 ± 0.02	87
62c–62f 71a–71d	525 nm 468 nm	Mb, and FTIR spectroscopy	525 nm: one (62d, 71b) 468 nm: three (62d, 71b)	62d: 1.91 ± 0.16 min 71b: 2.27 ± 0.27 min	DMSO DCM	62d: (0.60 ± 0.05) × 10 ⁻² s ⁻¹ 71b: (0.50 ± 0.05) × 10 ⁻² s ⁻¹		88
72a–72f	365 nm	FTIR			DMSO and DCM			89
73 and 74	365 nm		73: 2	73: 22.28 min	DMSO/PBS			90

3.1.2.6. Azo-pyridine photoCORMs								
75a and 75b	≥ 520 nm	Mb			DCM, CH ₃ CN 20 % (v/v) CH ₃ CN/H ₂ O	DCM: 75a: 21.94 ± 0.01 min ⁻¹ 75b: 15.28 ± 0.01 min ⁻¹ CH ₃ CN: 75a: 11.216 ± 0.01 min ⁻¹ 20 % (v/v) CH ₃ CN/H ₂ O: 75a: 4.987 ± 0.01 min ⁻¹	CH ₃ CN: 75a: 0.48 ± 0.01	91, 92
76a–76e	≥ 625 nm	Mb	In the dark 76a–76b: ≤ 0.1 equiv. 76c–76e: ≈ 0.7 equiv.	t _{1/2} (h) CH ₂ Cl ₂ 76a: 3.52 ± 0.06 76b: 3.60 ± 0.05 76c: 1.21 ± 0.14 76d: 0.48 ± 0.01 76e: 0.41 ± 0.01 DMSO 76a: 1.50 ± 0.05 76b: 1.13 ± 0.17 76c: 0.76 ± 0.05 (3.05 ± 0.30) ⁱ (0.85 ± 0.11) ⁱ 76d: 0.21 ± 0.01 (1.07 ± 0.02) ⁱ (0.50 ± 0.05) ⁱ 76e: 0.31 ± 0.01 (1.23 ± 0.03) ⁱ (0.54 ± 0.07) ⁱ	DMSO and DCM			93
3.1.2.7. Other <i>N,N</i> -bidentate photoCORMs								
77a–77l	365 and 480 nm	Portable CO sensor	Illumination for 30 min: 77a (solid phase): 0.086 (365 nm) and 0.089 (480 nm) CO/CORM		Solid state MeOH			94
78–81a	380 nm	FTIR and UV-vis spectroscopy as well as COP-1			DCM and CH ₃ CN	DCM 78: (3.0 ± 0.1) × 10 ⁻³ s ⁻¹ 79: (4.0 ± 0.1) × 10 ⁻³ s ⁻¹ 80: (4.9 ± 0.1) × 10 ⁻³ s ⁻¹ 81: (2.3 ± 0.1) × 10 ⁻³ s ⁻¹ CH ₃ CN 78: (1.3 ± 0.1) × 10 ⁻³ s ⁻¹ 79: (3.0 ± 0.1) × 10 ⁻³ s ⁻¹ 80: (1.0 ± 0.1) × 10 ⁻³ s ⁻¹ 81: (1.0 ± 0.1) × 10 ⁻³ s ⁻¹	DCM 78: ____ 79: 0.05 ± 0.01 80: 0.06 ± 0.01 81: 0.02 ± 0.01	95, 96
81a	307 nm 350 nm	Mb			CH ₃ CN	307 nm: (11.7 ± 0.2) × 10 ⁻² s ⁻¹ 350 nm: (5.2 ± 0.2) × 10 ⁻³ s ⁻¹	(5.2 ± 0.2) × 10 ⁻³	95

81b	468 nm	Mb	3 equiv.	17.28 ± 3.6 min	DMSO	$(7.0 \pm 0.10) \times 10^{-4} \text{ s}^{-1}$		97
82	365 nm	Mb	1.3 moles		DMSO			98
3.1.3. N,O-bidentate ligands								
83	400 and 465 nm	Mb	465 nm: 1.4 moles 400 nm: 2 moles		DMSO			99- 101
84 and 85	400–700 nm	Mb and IR spectroscopy			CH ₃ CN MeOH (Mb)	84: $(1.92 \pm 0.02) \times 10^{-3}$ and $(2.76 \pm 0.03) \times 10^{-3}$ 85: $(3.30 \pm 0.01) \times 10^{-3}$ and $(4.46 \pm 0.04) \times 10^{-3}$		103
86a and 86b	468 nm	Mb	DMSO: 86a: 2.75 ± 0.03 equiv. 86b: 2.33 ± 0.02 equiv. H ₂ O: 86a: 0.66 equiv. 86b: 1.31 equiv.	DMSO: 86a: 10.26 min 86b: 8.93 min H ₂ O: 86a: 5.4 min 86b: 5.2 min	DMSO H ₂ O	DMSO: 86a: $1.1 \times 10^{-3} \text{ s}^{-1}$ 86b: $1.3 \times 10^{-3} \text{ s}^{-1}$ H ₂ O: 86a: $2.1 \times 10^{-3} \text{ s}^{-1}$ 86b: $2.2 \times 10^{-3} \text{ s}^{-1}$		104
87	468 nm	Mb	3 equiv.	4.54 ± 0.17 min	DMSO	$(26.0 \pm 0.18) \times 10^{-3} \text{ s}^{-1}$		97
88	- UV (365–370 nm) - Blue (465–470 nm) - Green (520–530 nm)	- Mb - CO detector	Mb: UV: 2.3 moles Blue: 2.1 moles Green: 1.4 moles	Mb: UV: 7 min Blue: 37 min Green: 62 min	PBS	Mb: CO detector: (min ⁻¹) (g/mol.min) UV: 0.099 2.74 Blue: 0.019 2.07 Green: 0.011 1.11		49
3.1.4. N,S- and N,Se-bidentate ligands								
89	468 and 525 nm	Mb and CO sensor	CO sensor: 468 nm: 1.5 equiv. 525 nm: 1.0 equiv. Mb: 468 nm: 2.62 equiv. 525 nm: 1.70 equiv.	Mb: 468 nm: 1.0 ± 0.1 min 525 nm: 15.0 ± 0.2 min	DMSO	Mb: 468 nm: 0.01155 s ⁻¹ 525 nm: 0.00066 s ⁻¹		106
90a, 90b and 91	468 nm	Mb	90a–90b: 2 equiv. 91: one equiv.		DMSO			107
92–94	380 nm	*COP-1 UV IR NMR	3 COs		DCM, CH ₃ CN PBS, pH 7.4	UV: 92: $(1.82 \pm 0.03) 10^{-3} \text{ s}^{-1}$ 93: $(7.76 \pm 0.15) 10^{-3} \text{ s}^{-1}$ 94: $(7.87 \pm 0.15) 10^{-3} \text{ s}^{-1}$		108
95a–95d	365 nm (UV) 405 nm (purple) 435 nm (blue)	Mb	(equiv.) UV Purple Blue 95a: 2.04, 1.64, 1.08 95b: 2.43, 2.23, 1.24 95c: 2.17, 2.01, 1.85 95d: 2.05, 1.55, 1.32	(s) UV Purple Blue 95a: 11.03 8.46 92.31		(s ⁻¹) UV Purple Blue 95a: 0.0262, 0.0139, 0.00666 95b: 0.0121, 0.0138, 0.0181 95c: 0.0184, 0.0145, 0.00488 95d: 0.0195, 0.057, 0.0064		110

				95b: 12.47 17.20 95.75 95c: 12.69 46.28 56.81 95d: 44.54 59.59 65.90				
96	Insufficiently soluble for the Mb assay							111
3.1.5.1. Polynuclear photoCORMs								
3.1.5.1. Homonuclear photoCORMs								
97a, 97b and 98	410 nm	Mb	97a: 7.56 ± 0.02 equiv. 97b: 15.24 ± 0.15 equiv. 98: 1.51 ± 0.07 equiv.	97a: 14.54 ± 0.25 min 97b: 16.84 ± 0.56 min 98: 7.41 ± 0.24 min	10 % (v/v) DMSO/H ₂ O	97a: 0.000795 s ⁻¹ 97b: 0.000686 s ⁻¹ 98: 0.001558 s ⁻¹	97a: (2.66 ± 0.16) × 10 ⁻³ 97b: (2.71 ± 0.49) × 10 ⁻³ 98: (3.15 ± 0.27) × 10 ⁻³	113
99a–99h	470 nm	Mb and IR gas phase spectroscopy	Mb: 99a: 3 molecules ^l IR spectroscopy: Dark 2.37 ± 0.06 molecules Illumination 7.41 ± 0.31 molecules	IR spectroscopy: Dark 459 ± 80 s Illumination 750 ± 340 s	DMSO	IR spectroscopy: Dark 459 ± 80 s Illumination 750 ± 340 s		114
100	365 and 405 nm	Portable CO sensor and IR spectroscopy	CO sensor: (µmol/mg) 405 nm *100-PLA: 8.1–8.3 *100-PMMA: 11.0–11.7 365 nm: 100-PLA: 10.7 100-PMMA: 11.5–11.6		Solvent-free			115
101 and 102	365, 405, 470 and 480 nm	Mb and IR gas phase spectroscopy	101 (equiv.) Mb: 365 nm: 5.36 405 nm: 4.57 480 nm: 2.82 Gas IR spectroscopy: 365 nm: 6.4 ± 0.4 470 nm: 6.0 ± 0.5	101 Gas IR spectroscopy: 365 nm: 920 ± 90 s 470 nm: 920 ± 140 s	PBS			116
103 and 104	365 nm	Mb	104: 1.8 mol		DMSO			117 – 119
105a–105d	365 nm	Mb						120
106a–106h	365 nm	Mb	106e: 2.65 ± 0.13 moles 106f: 3.61 ± 0.089 moles					121

107a–107f	365 nm	Mb	107b : 2.89 ± 0.024 equiv.					122
108a and 108b	365 nm	Mb FTIR	Mb: 108a : 1.73 ± 0.21 equiv. 108b : 1.87 ± 0.05 equiv.	Mb: 108a : 9.21 × 10 ² min 108b : 3.27 × 10 ² min	DMSO			123
109a–109h	520–560 nm	Mb	109e : 3.83 ± 0.09 equiv. 109g : 3.18 ± 0.12 equiv.	109e : 5.37 × 10 ² s 109g : 5.82 × 10 ² s	PBS	109e : 1.29 × 10 ⁻³ s ⁻¹ 109g : 1.19 × 10 ⁻³ s ⁻¹		124
110	520–530 nm (Green) 465–470 nm (Blue) 365–370 nm (UV)	Mb	Green: 2.5 equiv. Blue: 2.9 equiv. UV: 2.8 equiv.	Green: 10 min Blue: 6 min UV: 2 min	PBS	Green: 0.069 min ⁻¹ Blue: 0.116 min ⁻¹ UV: 0.347 min ⁻¹		125
3.1.5.2. Heteronuclear photoCORMs								
111a–111d	Deep red (111a–111b) NIR (111c–111d)	GC-TCD	111b (mol): Aerobic CH ₃ CN: 2.28 ^k (453 nm), 2.01 ^k (659 nm), 1.96 ^l (659 nm) Anaerobic CH ₃ CN: < 0.09 ^k Anaerobic 90 % (v/v) CH ₃ CN/CHCl ₃ : < 0.07 ^k Aerobic CH ₂ Cl ₂ : 1.87 ^k		Aerobic CH ₃ CN Anaerobic CH ₃ CN 90 % (v/v) CH ₃ CN/ CHCl ₃ Aerobic CH ₂ Cl ₂			129
112 and 113	470 and 627 nm	FTIR and GC	3 equiv.		CH ₃ CN		Φ_{470}^m 112 : 0.37 ± 0.06 (0.22 ± 0.03) ⁿ 113 : 0.16 ± 0.03 (0.049 ± 0.008) ⁿ Φ_{627}^m 112 : 0.38 ± 0.04 113 : 0.13 ± 0.01	130
114a and 114b	470 nm	FTIR	114a : 3 COs were released		CH ₃ CN			131
115a–115f	365 nm	UV-vis. and FTIR spectroscopy			CH ₃ CN			132
3.1.6. Tridentate ligands								
3.1.6.1. Di-(2-picoly)amine based photoCORMs								
117, 118 and 119a–119c	365 nm	Mb	119a : 1.59 equiv. 119b : 2.65 equiv. 119c : 1.65 equiv.	20 min for all	DMSO			134

120	365 nm	Mb	365 nm: 3.2 ± 0.1 equiv. Dark incubation: 2.2 ± 0.1 equiv.		DMSO			136
121	365 nm	IR spectro-electrochemistry	3 COs		CH ₃ CN/ 0.1 M (Bu ₄ N)PF ₆			137
122a and 122b	410 nm	Mb		122a : 16.7 min 122b : 23.2 min	CH ₃ CN	122a : 0.0416 ± 0.0025 min ⁻¹ 122b : 0.02983 ± 0.00113 min ⁻¹	122a : 0.599 ± 0.036 122b : 0.426 ± 0.016	138
123 and 124	307 nm 350 nm	Mb		1.4–2.2 min	CH ₃ CN PBS	307 nm 123 : (9.1 ± 0.2) × 10 ⁻² s ⁻¹ 124 : (8.1 ± 0.2) × 10 ⁻² s ⁻¹ 350 nm 123 : (6.0 ± 0.2) × 10 ⁻³ s ⁻¹ 124 : CH ₃ CN: (8.3 ± 0.2) × 10 ⁻³ s ⁻¹ PBS: 5.6 × 10 ⁻³ s ⁻¹	123 : 0.07 ± 0.01 124 : 0.06 ± 0.01	95
124-Al-MCM-41	> 350 nm	Mb			PBS	124-Al-MCM-41 released CO more slowly than from 124 .		139
125 and 126	405 nm H ₂ O ₂	Mb	3 COs		Aqueous PBS			140
127	490 nm 470 nm 450 nm 413 nm 365 nm	Mb and Confocal laser scanning microscopy	Confocal laser scanning microscopy: 150 ppm at 470 nm		1% (v/v) (DMSO/ PBS)	490 nm: 5 min ⁻¹	365 nm: 8% 413 nm: 7.7% 450: 3.5 % 490 nm: 1.2%	141
128	405 nm	Mb	128 : 3 equiv. 128 entrapped on a paper strip: 1.5 μM mg ⁻¹		DMSO		1.5 ± 0.2%	142
129 and 130	two-photon laser beam (800 nm)	CO gas sensor	129 : 220 ppm 130 : 145 ppm 129 and 130 embedded in poly(L-lactide-co-D/L-lactide) nonwoven fabric material released about 22 and 10 ppm, respectively.		CH ₃ CN			143
131 and 132	550 nm	Mb, Solution IR and CO sensor	131 : Mb and Solution IR: 3 equiv. 132 : CO sensor: 50 ppm 132-PTFE : 45 ppm		2% (v/v) (DMSO/ PBS)	131–132 : 13 s ⁻¹		146
133–135	550–560 nm > 345 nm	UV-vis. and Gas chromatography	About 2.5 units	133 : 49.9 s At 345 nm: 133 : 6.8 s 135 : 1.7 min	CH ₃ CN	133 : 0.01389 s ⁻¹	At 475nm: 133 : 0.42 134 : 0.025	147

3.1.6.2. Pyrazolyl and imidazolyl photoCORMs								
136	365 nm	Mb IR spectroscopy	About 2 COs 3 COs		DMSO CH ₃ CN			149 - 152
137	365 nm	Mb	1.7 equiv.					153
138 and 139	365 nm	Mb	138a-138b : 2 moles 139a-139c : 1 mole		DMSO			155
140-143	365 nm	Mb	140 : 1.61±0.29 equiv. 141 : 1.37±0.08 equiv. 142 : 2.28±0.01 equiv. 143 : 1.04±0.28 equiv.	140 : 19 min 141 : 32 min 142 : 17 min 143 : 13 min	DMSO			156
144a-144c 145a-145b	365 nm 410 nm	Mb	144a : 2.3 ± 0.1 equiv. 144b : 2.5 ± 0.1 equiv. 144c : 2.3 ± 0.1 equiv. 145a : 2.1 ± 0.1 equiv. 145b : 2.1 ± 0.1 equiv.	144a : 21.6 ± 0.3 min 144b : 21.3 ± 0.5 min 144c : 18.5 ± 0.2 min 145a : 25.8 ± 0.2 min ^o 145b : 28.7 ± 0.8 min	DMSO	144a : 0.00642 s ⁻¹ 144b : 0.01060 s ⁻¹ 144c : 0.01208 s ⁻¹ 145a : 0.00783 s ⁻¹ 145b : 0.00745 s ⁻¹	144a : (5.9 ± 0.2) × 10 ⁻³ 144b : (6.3 ± 0.4) × 10 ⁻³ 144c : (6.6 ± 0.1) × 10 ⁻³ 145a : (4.4 ± 0.2) × 10 ⁻³ 145b : (4.3 ± 0.2) × 10 ⁻³	157
146, 147 and 148a and 148b	365 nm	Mb - 146 : IR spectroscopy ¹⁵¹	146-147, 148a : ≈ 2 equiv. 148b : 1.42 ± 0.04 equiv. 146 : 3 COs ¹⁵¹	146 : 6.73 min 147 : 11.35 min 148a : 3.77 min 148b : 217 min	DMSO 146 : CH ₃ CN ¹⁵¹			44, 151 158 , 159
149	405 nm 470 nm	Mb and IR gas phase spectroscopy	IR: 405 nm: 2.92 ± 0.45 CO 470 nm: 2.79 ± 0.56 CO Mb: 2 COs	IR: 405 nm: 408 ± 81 s 470 nm: 1950 ± 310 s	PBS			161
3.1.6.3. Other tridentate based photoCORMs								
150	365 nm	Mb	1 equiv.	93.0 ± 9.2 min	DMSO			111
151 and 152	365 nm 405 nm 380 nm	- IR gas phase spectroscopy - Mb	IR, at 365 nm: 151 : 2.86 ± 0.28 CO 152 : 2.61 ± 0.12 CO		PBS	Myoglobin, at 380 nm: 151 : 236 ± 24 s 152 : 384 ± 6 s		162
3.1.7. Drug based photoCORMs								
153	525 nm 468 nm	Mb	525 nm: 1 equiv. 470 nm: 2.85 equiv.		DMSO			163
154 and 155	412-468 nm	Mb	155 : 0.5 equiv. (410 nm), < 0.5 equiv. (468 nm)		DMSO			164

3.2. Tetracarbonyl Mn(I) photoCORMs								
156a and 156b	365–400 nm	Mb	3 COs	365 nm: 156a : 960 s (40 μ M) 156b : 1740 s (40 μ M) 400 nm: 156a : 300 s (10 μ M), 360 s (40 μ M)	DMSO			165
157a–157f	365 nm 400 nm	Mb (365 nm)	157c, 157d : 3 COs	157a : 23 min 157b : 17 min 157c : 27 min 157d : 18 min 157e : 30 min 157f : 14 min				166
158–162	400 nm	Mb	158, 159 : about 3 COs 162 : 2.5 equiv.		DMSO			167
4. Thermal and redox Mn(I) CORMs								
4.1. CORM-401								
163	Spontaneous	Mb ^{168, 169} GC ¹⁶⁸	Mb: 3.2 equiv. ¹⁶⁹ GC: 0.33 equiv. ¹⁶⁹ 3 COs ¹⁶⁸	0.8 min ¹⁶⁹	PBS ^{168, 169}			168 169
4.2. Other Mn(I) CORMs								
165–168	Spontaneous	Hemoglobin assay		165 : 11.1 min 166 : 8.6 min 167 : 11.3 min 168 : 65 min	Aqueous solutions			207
169	100 W Xe arc lamp 355 nm	Time-resolved IR			THF CH ₃ CN			209
170–172	Thermally and 400 nm	Mb			H ₂ O			210

^a CORM-1 reduces acute hypertension and coronary vasoconstriction in rats.

^b Complexes **1a** and **1b** released 1.1 ± 0.1 ($t_{1/2} = 124$ min) and 2 ($t_{1/2} = 73$ min) equivalents, respectively of CO under dark conditions upon dissolution in aqueous media.

^c Complex **7** can block the release of NO and TNF- α in LPS-stimulated RAW264.7 macrophages without clear cytotoxicity.

^d Along with an increase in concentration and CO release, antioxidant activities of **17a** and **17b** have also grown.

^e When F⁻ ions are present, the rate of CO release is rapid and has a $t_{1/2} < 1$ (0.8608) min ($k_{CO} = 0.805$ min⁻¹).

^f Upon illumination of **39** at 525 nm, approximately 4 equivalents of CO were released.

^g The k_{CO} values of **63** in DCM and CH₃CN were 19.7 ± 0.2 ($t_{1/2} = 15.2$ s) and 16.9 ± 0.2 min⁻¹ upon illumination at 520 nm, respectively.

^h The k_{CO} values of **65** were 5.11 ± 0.02 min⁻¹ using light with power of 10 mW/cm² and 2.35 ± 0.02 min⁻¹ using power of 1 mW/cm².

ⁱ Under dark conditions.

^j Prior to illumination, **99a** released 0.1 molecule of CO/CORM under dark conditions.

^k 2.75 mM, ^m 0.13 mM.

^l PF₆⁻ salts of the complexes in CH₃CN at ambient temperature.

^m Cl⁻ salts of the complexes in H₂O at ambient temperature.

ⁿ Upon illumination at 410 nm, the t_{1/2} value reached to 132 min as a result of the poor absorption at this higher wavelength.

^o The quantity of CO released by CORM-401 increased in presence of oxidants.

*Abbreviations:

Mb: myoglobin assay.

FTIR: Fourier transform infrared spectroscopy.

TA: time-resolved.

EPR: electron paramagnetic resonance.

GC: Gas chromatography.

TCD: thermal conductivity detector.

COP-1: carbon monoxide Probe 1.

PLA: poly(L-lactide-co-D/L-lactide).

PMMA: poly(methyl methacrylate).

Table 2 Antimicrobial properties of the tested Mn(I) carbon monoxide releasing molecules.

CORM	Activation wavelength	Bacteria/Fungi	Antimicrobial/Antifungal activity	Ref.
3.1.1. Monodentate ancillary ligands				
3a–3f	350 nm	<i>Escherichia coli</i>	<ul style="list-style-type: none"> All 3a–3f, except for 3d exhibited no antibacterial activity. MIC = 128 µg/mL in the dark and 256 µg/mL if light induced 	46
3.1.2. N,N-bidentate ligands				
3.1.2.1. 2,2'-Bipyridine photoCORMs				
17a and 17b	365 nm	<i>Escherichia coli</i> , <i>Bacillus subtilis</i> , <i>Micrococcus luteus</i> , <i>Pseudomonas aeruginosa</i> , <i>Klebsiella pneumoniae</i> , and <i>Listeria monocytogenes</i> . <i>Candida albicans</i> and <i>Aspergillus niger</i> .	<ul style="list-style-type: none"> Both displayed moderate to strong antimicrobial activity against some strains. 17a exhibited antifungal activity against <i>Candida albicans</i> and <i>Aspergillus niger</i>, in the dark. Antioxidant activities of 17a and 17b have been grown after illumination. 	57
3.1.2.2. 1,10-Phenanthroline photoCORMs				
23 and 24	365–555 nm	<i>Escherichia coli</i>	<ul style="list-style-type: none"> While 23d did not inhibit <i>E. coli</i> from growing, the photolyzed solution completely suppresses the bacterial growth. The toxicity had been attributed to the presence of phenanthroline species. 	61
28–30	435–450 nm	Multi-drug resistant bacteria	<ul style="list-style-type: none"> The toxicity appears to be related to the combination of CO release and iCORM, based on the difference in toxicity under light and dark settings. 30 displayed poor antibacterial activity at low doses, however it was active only at ≥ 128 µg/mL against the Gram-negative bacteria. They were only mildly harmful to <i>Galleria mellonella</i>. 	67
3.1.2.3. $\kappa^2N^1N^2$- terpyridine photoCORMs				
37–42	468 nm 525 nm	<i>Escherichia coli</i> , <i>Candida albicans</i> <i>Candida neoformans</i>	<ul style="list-style-type: none"> 41 displayed toxicity to <i>Escherichia coli</i> with MIC value of 8 µg/mL. All compounds exhibited antifungal activities against <i>C. albicans</i> and <i>C. neoformans</i> (MIC = 4–32 µg/mL). 	74

3.1.2.5. <i>N,N</i> -Schiff-base photoCORMs				
68	468 nm 525 nm	<i>Candida albicans</i> <i>Candida neoformans</i>	<ul style="list-style-type: none"> 68 displayed antifungal activity (16 µg/mL) against <i>C. albicans</i> and <i>C. neoformans</i> in the dark. 68 was harmful to the HEK-293 with CC₅₀ of 12.56 µg/mL. 	86
3.1.3. <i>N,O</i> -bidentate ligands				
83	400 and 465 nm	<i>E. coli</i> W3110	<ul style="list-style-type: none"> <i>E. coli</i> W3110 cell growth is inhibited by 83 after only irradiation. When 83 is pre-irradiated before the addition of <i>E. coli</i> W3110 cells, the growth profile of the bacteria is like that observed in the absence of CORM indicating that the bactericidal effect is caused by in situ breakdown of the CORM in the presence of cells. Both 83 and its iCORM are not toxic to the tested bacteria. 	99-101
3.1.4. <i>N,S</i> - and <i>N,Se</i> -bidentate ligands				
95a-95d	365-435 nm	<i>Corynebacterium diphtheriae</i> , <i>Yersinia enterocolitica</i> and <i>Micrococcus luteus</i> .	<ul style="list-style-type: none"> The complexes may inhibit the growth of the tested microbes. Blue light significantly improves their antibacterial properties. iCORMs were inactive than the parent compounds. The CO release brought on by irradiation is what caused the growth inhibition. 	110
3.1.6. Tridentate ligands				
3.1.6.1. Di-(2-picolyl)amine based photoCORMs				
120	365 nm	<i>Escherichia coli</i>	<ul style="list-style-type: none"> Upon illumination, a pronounced and concentration-dependent reduction in the rate of treated <i>E. coli</i> growth was seen when using medium with succinate (the only carbon source) was observed. 	136
133-135	550-560 nm > 345 nm	<i>Escherichia coli</i>	<ul style="list-style-type: none"> Against <i>E. coli</i>, the loaded non-woven fabric demonstrated substantial reductions in bacterial growth after being exposed to light for 6 h. 	147
4. Thermal and redox Mn(I) CORMs				
4.1. CORM-401				
163	Spontaneousl y	<i>Escherichia coli</i> <i>Pseudomonas aeruginosa</i>	<ul style="list-style-type: none"> 163 inhibits bacterial growth when used in conjunction with cefotaxime and trimethoprim, studies on fractional inhibition show no interaction. 	194

			<ul style="list-style-type: none">• The resistance of <i>P. aeruginosa</i> to 163 may be due the failure of these bacteria to accumulate 163 intracellularly.	
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Table 3 Cytotoxic properties of Mn(I) carbon monoxide releasing molecules

CORM	Activation wavelength	Cell line *	Cytotoxic activity	Ref.
3.1.1. Monodentate ancillary ligands				
2	468 nm	THP-1 and BM.	<ul style="list-style-type: none"> Under dark conditions, 2 showed mild selective cytotoxic effect with $IC_{50} = 68.02 \pm 5.7$ $\mu\text{g/mL}$ THP-1, and no negative effects were observed against BM cells. The cytotoxicity of 2 did not largely alter upon the illumination with $IC_{50} = 72.62 \pm 5.6$ $\mu\text{g/mL}$. Upon illumination 2 caused extreme cytotoxicity against BM cells with $IC_{50} = 4.67 \pm 0.2$ $\mu\text{g/mL}$. 	45
3a–3f	350 nm	3T3 fibroblasts	<ul style="list-style-type: none"> When incubated at 100 μM, 3a–3f showed a distinct toxic effect in the dark and under light conditions. 	46
3.1.2. N,N-bidentate ligands				
3.1.2.1. 2,2'-Bipyridine photoCORMs				
7	Green, blue, and UV light	RAW264.7 macrophages	<ul style="list-style-type: none"> Both 7 and its iCORM are almost non-toxic. 7 can block the release of NO and TNF-α in LPS-stimulated RAW264.7 macrophages without clear cytotoxicity. 	49
13a, 13b, 14, 15a and 15b	365 nm	MCF-7	<ul style="list-style-type: none"> IC_{50} (μM) values upon illumination are 3.1 ± 0.1, 21 ± 1, 10 ± 1, 2.91 ± 0.07 and 9.7 ± 0.6 in that order. 	55
16a–16e	365 nm	MCF-7	<ul style="list-style-type: none"> 16a–16e displayed enhanced antiproliferation properties upon illumination. IC_{50} (μM) values upon illumination were 2.91, 12.25, 1.79, 1.43 and < 1, respectively. 	56
3.1.2.2. 1,10-Phenanthroline photoCORMs				
21 and 22	Low-power visible light	HEK-293 and HT29	<ul style="list-style-type: none"> HT29 cells are eradicated with 100 μM of 21 or 22, leading to a drop to 10–48 % when exposed to visible light. No toxicity against HEK-293 cells. 	59, 60
25	Low power (10 mW/cm ²) visible light	OVCAR-5 and SKOV-3	<ul style="list-style-type: none"> The CO alone was responsible for the cytotoxicity, and the targeted delivery of CO required the presence of the appropriate antigen on the surface of the cancer cells. Neither 25 in the dark nor the light-inactivated 25 resulted in any substantial cell death. 	62
26, 26-B₁₂	420 nm	MCF-7	<ul style="list-style-type: none"> In the dark, the B₁₂ conjugated photoCORMs display a lower toxicity than the corresponding parents. 	63

			<ul style="list-style-type: none"> Comparing the toxicity levels of the dark and light studies revealed that there were no noticeable changes or trends. 	
27b	low-power visible light	MDA-MB-231	<ul style="list-style-type: none"> 100 μM of 27b reduced the cell viability by about 50% upon illumination. 	66
3.1.2.3. $\kappa^2N^1N^2$- terpyridine photoCORMs				
37–42		HEK-293	<ul style="list-style-type: none"> 37 experienced serve cytotoxicity to normal HEK-293 with IC_{50} of 4.878 $\mu\text{g}/\text{mL}$. 	74
3.1.2.4. Benzimidazole and benzothiazole photoCORMs				
43a⁷⁵, 44⁷⁷, 51⁷⁸, 52⁷⁸	365 nm	SK-Hep1 and HL-7702	<ul style="list-style-type: none"> Bright green fluorescence is detected in cells after incubation with 51 and 52. 51 has superior anticancer activity against SK-Hep1 cells. 	75, 77, 78
57	Low power (15 mW/cm^2) visible light	MDA-MB-231	<ul style="list-style-type: none"> iCORM is nontoxic. 100 μM of 57 reduce the cell viability by about 50% upon illumination. 	66
58 and 59	low-power (mW levels)	HT-29 and HEK-293	<ul style="list-style-type: none"> The CO-catheter could be used to administer CO to cancerous areas during adjuvant treatment for colon cancer. 	82
3.1.2.5. <i>N,N</i>-Schiff-base photoCORMs				
68	468 nm 525 nm	HEK-293	<ul style="list-style-type: none"> 68 was harmful with CC_{50} of 12.56 $\mu\text{g}/\text{mL}$. 	86
69 and 70	15 mW visible light	HT-29	<ul style="list-style-type: none"> When irradiated, both 69 ($\text{IC}_{50} = 40 \mu\text{M}$) and 70 ($\text{IC}_{50} = 70 \mu\text{M}$) gained cytotoxicity. The free ligands, and their iCORMs are nontoxic in the dark. 	87
62c–62f 71a–71d	525 nm 468 nm	HepG2	<ul style="list-style-type: none"> The CORMs were inactive against HepG2 cells in the dark. When exposed to light, 62c, 62d, 71a and 71b released CO in a comparable way, but their impact on the cell viability was very different, indicating that the iCORM was the primary cause of the cytotoxicity. 62d ($\text{IC}_{50} = 7.1 \mu\text{M}$) showed the highest phototoxicity. 	88
72a–72f	365 nm	HepG2	<ul style="list-style-type: none"> 72b and 72d are inactive in the dark, 72a and 72c demonstrate cytotoxicity, with IC_{50} values of 18.1 and 11.8 μM, respectively. The cytotoxicity of 72a and 72c increased with illumination, $\text{IC}_{50} = 7.9$ and 6.6 μM. The inactive compounds turned active upon illumination, $\text{IC}_{50} = 5.7 \mu\text{M}$ (72b) and 6.7 μM (72d). The nitro derivatives 72e and 72f are inactive before and after illumination. Synergistic effect between iCORM and CO. 	89
3.1.2.6. Azo-pyridine photoCORMs				
75a and 75b	$\geq 520 \text{ nm}$	HeLa and MDA-MB-231	<ul style="list-style-type: none"> 75 μM of 75a and illumination time of 10 min caused about 60% reduction in the cell viability. 	91, 92

3.1.2.7. Other <i>N,N</i> -bidentate photoCORMs				
81b	468 nm	HEK-293T and MDA-MB-231	<ul style="list-style-type: none"> 81b exhibits significant cytotoxicity both in the dark and when exposed to light, with IC₅₀ values of 19.62 and 11.43 μM, respectively. It displayed the same cytotoxic pattern against the normal HEK-293T. The cell viability of the co-treated cells is much lower than that of the cells treated only with Paclitaxel drug and lower than that of the cells treated with 82. 	97
82	365 nm	HCT-15, A549 and HeLa	<ul style="list-style-type: none"> 82 displayed a photocytotoxicity with IC₅₀ values of 7.15 ± 0.24, 12.5 ± 1.33, and 20.7 ± 0.94, respectively. 	98
3.1.3. <i>N,O</i> -bidentate ligands				
84 and 85	400–700 nm 350 nm	HeLa	<ul style="list-style-type: none"> The complexes were non-cytotoxic in the dark (IC₅₀ > 50 μM). After 30 min of illumination, both complexes reduced the cell viability with IC₅₀ values in the range of 7.29–36.05 μM. 	103
86a and 86b	468 nm	HEK-283T, MDA-MB-231 and SW-620.	<ul style="list-style-type: none"> 86a and 86b had no effect up to 50 μM. 	104
87	468 nm	HEK-283T and MDA-MB-231.	<ul style="list-style-type: none"> 87 is inactive up to 50 μM against MDA-MB-231 under both dark and light conditions. 	97
88	- UV (365–370) - Blue (465–470) - Green (520–530) nm	RAW264.7	<ul style="list-style-type: none"> 88 and its iCORM are almost non-toxic. It can block the release of NO and TNF-α in LPS-stimulated RAW264.7 macrophages without obvious cytotoxicity. 	49
3.1.4. <i>N,S</i> - and <i>N,Se</i> -bidentate ligands				
95a–95d	365–435 nm	A549 and HEK-293T.	<ul style="list-style-type: none"> In a dose-dependent manner, 95a–95d and their iCORMs exhibit cytotoxic effects. The cytotoxicity was not significantly changed by irradiation. The cytotoxicity of 95b against HEK293T cells was increased by blue light irradiation. 	110
3.1.5. Polynuclear photoCORMs				
3.1.5.1. Homonuclear photoCORMs				
103 and 104	365 nm	A549, HeLa, MDA MB-231, HCT-15 and HEK-293	<ul style="list-style-type: none"> Upon illumination, 103 was cytotoxic against HCT-15 and A549 cells with IC₅₀ values of 28.7 ± 0.16 and 15.7 ± 0.98 μM, respectively. Upon illumination, 104 exhibited broad-spectrum inhibitory effects against HCT-15, HeLa, A549 and MDA MB-231 cells with low IC₅₀ values of 15.4 ± 0.67 (HeLa), 15.8 ± 1.75 (A549) and 14.5 ± 0.97 (HCT-15). 	117– 119

			<ul style="list-style-type: none"> Upon illumination, 104 also showed IC₅₀ (μM) values of 21.37 ± 1.72 (A549), 24.12 ± 1.03 (HeLa), 21.89 ± 0.59 (MDA MB-231), and 13.69 ± 0.91 (HCT-15). 104 showed low toxicity against normal HEK-293 cells (> 50 μM). 	
105a–105d	365 nm	HEK-293, HCT-15, HeLa and A549.	<ul style="list-style-type: none"> 105b: minimum action on HCT-15 (13.18 ± 2.57 μM) and HeLa (12.05 ± 3.12 μM) cells, but potent against A549. 105c: at 365 nm, displayed potency (IC₅₀ = 11.41–33.12 μM) against malignant cell lines. 105c triggers cellular machinery related to apoptosis. It showed no toxicity against HEK-293 cells. 105d: minimum toxicity toward all tested cells. 	120
106a–106h	365 nm	HEK-293, A549, HCT-15 and HeLa.	<ul style="list-style-type: none"> 106f was the most potent compound against lung (IC₅₀ = 6.74 ± 1.77), cervical (IC₅₀ = 4.92 ± 0.89), and colon (IC₅₀ = 2.54 ± 0.579) cancer cells 106f was not toxic against normal HEK-293 cells. 	121
107a–107f	365 nm	HeLa, A549, HCT-15 and HEK-293	<ul style="list-style-type: none"> 107b exhibited cytotoxicity with IC₅₀ values in the range of 1.78–50.38 μM in the dark against cancer cells and no effect on HEK-293 cells. 107c and 107f exhibited selective cytotoxic effect against HCT-15 and HeLa cells with IC₅₀ = 31.14 ± 3.81 μM and 5.05 ± 0.76 μM, respectively. 107d showed cytotoxicity against HeLa, A549 and HCT-15 cells with IC₅₀ = 4.23 ± 0.56, 23.37 ± 1.41 and 16.38 ± 1.94 μM, respectively. 	122
109a–109h	520–560 nm	HeLa, HCT-15, A549 and HEK-293.	<ul style="list-style-type: none"> Under dark conditions, apoptosis was induced by 109e and 109g treatment to the cancer cells. 	123
110	520–530 (Green) 465–470 (Blue) 365–370 (UV) nm	RAW264.7	<ul style="list-style-type: none"> 110 and its iCORM did not substantially reduce the cell viability. 110 prevented LPS-stimulated RAW264.7 macrophages from secreting NO and TNF-α without clearly cytotoxic side effects. 	125
3.1.5.2. Heteronuclear photoCORMs				
115a–115f	365 nm	HEK-293T.	<ul style="list-style-type: none"> 115a and 115c exhibited strongest cytotoxicity against HEK-293T with LD₅₀ ≥ 10 μM. The rest of the complexes showed weaker cytotoxicity in the range of 20–40 μM. 	132
3.1.6. Tridentate ligands				
3.1.6.1. Di-(2-picolyl)amine based photoCORMs				
117, 118 and 119a–119c	365 nm	HCT116 and HepG2	<ul style="list-style-type: none"> Under both dark and illumination conditions, 118, 119a and 119b exhibited no cytotoxicity. 117 and 119c displayed cytotoxicity that is not related to the CO-releasing process. When irradiated, the IC₅₀ values of 117 in HCT116 and HepG2 cells were (50 ± 21) and (60 ± 13), while in the dark were (41 ± 6) and (61 ± 10), respectively. 	134

			<ul style="list-style-type: none"> The copolymer 117 exhibited cytotoxicity, whereas neither the bpma ligands nor the polymer exhibited significant cytotoxicity. 	
127	490, 470, 450, 413 and 365 nm	HepaRG [®] and LX-2.	<ul style="list-style-type: none"> Up to a dose of 250 μM, 127 and its iCORM revealed no cytotoxic effects against the tested cells. 	141
128	405 nm	LX-2 and HepaRG [®]	<ul style="list-style-type: none"> 128 exhibited moderate cytotoxicity to LX-2 and HepaRG[®] ($IC_{50} \approx 30$ nM). 	142
129 and 130	Two-photon laser beam (800 nm)	HeLa and LX-2	<ul style="list-style-type: none"> The complexes were non-toxic to both cell lines even at higher concentrations. 	143
131 and 132	550 nm	HEK cells	<ul style="list-style-type: none"> Both 131 and 132 showed lower cytotoxicity toward HEK cells than their iCORMs. 	146
133–135	550–560 nm > 345 nm	L929 and C6.	<ul style="list-style-type: none"> Under low intensity light exposure, the non-woven fabric significantly killed C6 cancer cells while exhibiting minimal toxicity to 1929 cell lines. 	147
3.1.6.2. Pyrazolyl and imidazolyl photoCORMs				
136	365 nm	HT-29	<ul style="list-style-type: none"> 136 exhibits photoinitiated cytotoxicity, resulting in a decrease in cell biomass by 30%. 	149, 150
149	405 nm 470 nm	LX-2 and HepaRG [®]	<ul style="list-style-type: none"> 149 exhibited no cytotoxic effects on HepaRG[®] and LX-2 at concentrations < 63 μmol L⁻¹. HepaRG[®] ($EC_{50} = 100$ μmol L⁻¹) was discovered to be more responsive to 149 than LX-2 ($EC_{50} = 146$ μmol L⁻¹) 	161
3.1.6.3. Other tridentate based photoCORMs				
151 and 152	365 nm 405 nm 380 nm	LX-2 and HepaRG [®]	<ul style="list-style-type: none"> Both complexes were found to be non-toxic for HepaRG[®] or LX-2 cells. Unlike 151, complex 152 accumulates in cells enabling administration of CO inside of cells. 	162
3.2. Tetracarbonyl Mn(I) photoCORMs				
156a and 156b	365–400 nm	Murine RAW 264.7 macrophages	<ul style="list-style-type: none"> 156a was viable at 10 μM, but when exposed to light, the cell viability was reduced to 80%. 156b and its iCORM displayed no cytotoxicity. The LDH assay showed that 156a and 156b did not induce the release of LDH up to 100 μM. 	165
158–162	400 nm	Murine RAW 264.7 macrophages	<ul style="list-style-type: none"> At 50 μM, 159 exhibited a low level of cytotoxicity, and at 100 μM, it significantly reduced cell viability. The photo by-products of 158 and 159 had no influence on the cell viability and LDH release. 	167

			<ul style="list-style-type: none"> Transformation of 159 into 160 during the assay may be the cause of this toxicity. 161 was safe to RAW 264.7 cells at 50 μM. Under dark and light condition, 162 is not toxic. 	
4. Thermal and redox Mn(I) CORMs				
4.1. CORM-401				
163	Spontaneous	Murine RAW264.7 macrophages, hLMVEC and MDA-MB-231-luc2-tdTomato.	<ul style="list-style-type: none"> 100 μM of 163 decreased the cell viability by 25%. The amount of nitrite formed in response to treatment of lipopolysaccharide was decreased by 70%. Breast cancer cell transmigration through hLMVEC was significantly reduced by 163 and PAPA NONOate alone or in combination. 	168, 170
4.2. Other Mn(I) CORMs				
164		HeLa	<ul style="list-style-type: none"> With $\text{IC}_{50} = 402.86 \mu\text{M}$, 164 was cytotoxic against HeLa cells. 	206

*Cell lines:

THP-1: human leukemia monocytic cells. BM: bone marrow cells. 3T3 fibroblasts: cells of murine embryonic fibroblasts. RAW264.7 macrophages: macrophages derived from a tumour created by the Abelson mouse leukemia virus in a male mouse. MCF-7: breast cancer cells. HEK-293: human embryonic kidney cells. HT29: colorectal adenocarcinoma.

OVCAR-5: metastatic gastrointestinal carcinoma. SKOV-3: human ovarian cancer cells. MDA-MB-231: triple negative breast cancer cells. SK-Hep1: hepatic adenocarcinoma.

HL-7702: human liver cells. HepG2: hepatocarcinoma. HeLa: cervical cancer cells. HCT-15: human colon cancer cells. A549: lung cancer cells. SW-620: colorectal cancer cells. HCT116: human colorectal cancer cells. HepaRG®: Parenchymal hepatocyte-like cells. LX-2: non-parenchymal hepatic stellate cell-like cells. L929: NCTC clone 929 of strain L.

C6: rat glioma cells. hLMVEC: human lung microvascular endothelial cells. MDA-MB-231-luc2-tdTomato: human breast cancer cells.

Note: The citation of the references in the table matches the information provided in the main article.