Discrete polynuclear manganese(II) complexes with thiacalixarene ligands: synthesis, structures and photophysical properties†

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Electronic Supporting Information

CCDC reference number 1050380.

Crystal data

$C_{80}H_{88}FMn_4O_{24}S_8 \cdot C_{14}H_{30}KO_8 \cdot 2(CH_4O)$	$Z = 1$
$M_r = 2358.31$	$F(000) = 1230.000$
Triclinic, $P\bar{1}$	$D_x = 1.502$ Mg m^{-3}
Hall symbol: $P\bar{1}$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 12.0143$ (9) Å	Cell parameters from 19966 reflections
$b = 12.3064$ (7) Å	$\theta = 3.5–29.4°$
$c = 18.2691$ (8) Å	$\mu = 0.76$ mm^{-1}
$\alpha = 101.431$ (4)°	$T = 100$ K
$\beta = 99.543$ (6)°	Plate, colorless
$\gamma = 90.807$ (5)°	0.26 × 0.24 × 0.09 mm
$V = 2607.8$ (3) Å^3	

Data collection

Xcalibur, Atlas, Gemini ultra diffractometer	13313 independent reflections
Radiation source: Enhance (Mo) X-ray Source	10415 reflections with $I > 2.0\sigma(I)$
Graphite monochromator	$R_{int} = 0.067$
Detector resolution: 10.4685 pixels mm^{-1}	$\theta_{max} = 29.5°$, $\theta_{min} = 2.9°$
ω scans	$h = -16 \rightarrow 16$
Absorption correction: analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.33 (release 27-03-2014 CrysAlis171 .NET) (compiled Mar 27 2014,17:12:48) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$k = -16 \rightarrow 16$
$T_{min} = 0.843$, $T_{max} = 0.940$	$l = -25 \rightarrow 23$
67424 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.052$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.125$	Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = $1.0/[A_0*T_0(x) + A_1*T_1(x) \cdots + A_{n-1}]*T_{n-1}(x)]$ where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 463. 674. 348. 88.5
$S = 0.98$	$(\Delta/\sigma)_{max} = 0.001$
13282 reflections	$\Delta\rangle_{max} = 1.24$ e Å^{-3}
710 parameters	$\Delta\rangle_{min} = -0.95$ e Å^{-3}
2 restraints	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.45212 (4)	0.32580 (4)	0.49935 (3)	0.0166	
F2	0.5000	0.5000	0.5000	0.0163	
Mn3	0.32300 (4)	0.54240 (4)	0.49771 (3)	0.0170	
O4	0.61314 (19)	0.36636 (18)	0.58294 (13)	0.0196	
C5	0.6556 (3)	0.3406 (2)	0.64741 (19)	0.0183	
C6	0.5963 (3)	0.2734 (3)	0.68488 (19)	0.0192	
S7	0.45234 (7)	0.23240 (6)	0.65371 (5)	0.0190	
O8	0.42726 (19)	0.20842 (17)	0.57177 (14)	0.0202	
O9	0.4267 (2)	0.14429 (19)	0.69048 (14)	0.0232	
C10	0.3780 (3)	0.3484 (3)	0.6898 (2)	0.0219	
C11	0.3382 (3)	0.4296 (2)	0.64657 (19)	0.0183	
O12	0.35330 (19)	0.42667 (18)	0.57757 (13)	0.0197	
C13	0.2772 (3)	0.5128 (3)	0.6875 (2)	0.0211	
S14	0.21702 (6)	0.62428 (6)	0.65031 (5)	0.0190	
O15	0.19683 (19)	0.59531 (19)	0.56848 (14)	0.0219	
O16	0.1211 (2)	0.65542 (19)	0.68606 (14)	0.0234	
C17	0.6804 (3)	0.2651 (2)	0.31850 (19)	0.0192	
C18	0.5874 (3)	0.2534 (2)	0.35613 (19)	0.0180	
O19	0.57444 (19)	0.31776 (18)	0.41971 (14)	0.0202	
C20	0.5103 (3)	0.1636 (3)	0.3164 (2)	0.0201	

S21	0.37967 (6)	0.13984 (6)	0.34455 (5)	0.0184	
O22	0.39283 (19)	0.16503 (17)	0.42655 (13)	0.0193	
O23	0.3370 (2)	0.02955 (18)	0.30718 (14)	0.0224	
C24	0.2876 (3)	0.2335 (3)	0.30675 (19)	0.0197	
C25	0.2375 (3)	0.1939 (3)	0.2316 (2)	0.0221	
C26	0.1625 (3)	0.2535 (3)	0.1912 (2)	0.0237	
C27	0.1378 (3)	0.3560 (3)	0.2315 (2)	0.0227	
C28	0.1875 (3)	0.3980 (3)	0.30581 (19)	0.0195	
C29	0.2683 (3)	0.3400 (2)	0.34869 (19)	0.0180	
O30	0.31566 (18)	0.37943 (17)	0.41822 (13)	0.0190	
S31	0.14426 (6)	0.53215 (6)	0.34188 (5)	0.0190	
C32	0.7669 (3)	0.3754 (2)	0.68770 (19)	0.0190	
C33	0.8116 (3)	0.3454 (3)	0.75512 (19)	0.0210	
C34	0.7523 (3)	0.2787 (3)	0.7899 (2)	0.0233	
C35	0.6433 (3)	0.2436 (3)	0.7524 (2)	0.0225	
H351	0.5997	0.1985	0.7733	0.0271*	
C36	0.8059 (3)	0.2485 (3)	0.8646 (2)	0.0331	
C37	0.7194 (4)	0.1898 (4)	0.8984 (3)	0.0491	
H371	0.7555	0.1740	0.9462	0.0736*	
H372	0.6916	0.1210	0.8643	0.0736*	
H373	0.6558	0.2353	0.9061	0.0739*	
C38	0.8522 (4)	0.3551 (4)	0.9218 (2)	0.0398	
H383	0.8782	0.3394	0.9707	0.0596*	
H382	0.7931	0.4072	0.9261	0.0601*	
H381	0.9141	0.3880	0.9050	0.0597*	
C39	0.9024 (4)	0.1717 (4)	0.8508 (3)	0.0451	
H391	0.9368	0.1525	0.8980	0.0677*	
H392	0.8737	0.1057	0.8144	0.0676*	
H393	0.9592	0.2076	0.8311	0.0678*	
H331	0.8847	0.3719	0.7787	0.0244*	
O40	0.16218 (19)	0.55216 (19)	0.42352 (14)	0.0216	
O41	0.0312 (2)	0.5416 (2)	0.30351 (15)	0.0242	
H271	0.0851	0.3975	0.2071	0.0268*	
C42	0.1071 (3)	0.2125 (3)	0.1084 (2)	0.0279	
C43	0.1238 (4)	0.3021 (3)	0.0629 (2)	0.0366	
C44	-0.0193 (4)	0.1892 (4)	0.1046 (3)	0.0447	
H443	-0.0560	0.1654	0.0524	0.0668*	
H441	-0.0541	0.2540	0.1281	0.0671*	
H442	-0.0302	0.1309	0.1308	0.0670*	
C45	0.1588 (5)	0.1071 (4)	0.0721 (3)	0.0484	

H451	0.1215	0.0828	0.0201	0.0727*	
H452	0.2380	0.1208	0.0733	0.0728*	
H453	0.1496	0.0490	0.0998	0.0729*	
H251	0.2559	0.1237	0.2078	0.0272*	
C46	0.5266 (3)	0.0934 (3)	0.2500 (2)	0.0240	
C47	0.6187 (3)	0.1062 (3)	0.2157 (2)	0.0267	
C48	0.6949 (3)	0.1945 (3)	0.25149 (19)	0.0219	
H481	0.7581	0.2065	0.2303	0.0259*	
C49	0.6435 (3)	0.0276 (3)	0.1441 (3)	0.0451	
C50	0.5493 (5)	-0.0603 (4)	0.1120 (3)	0.0572	
H502	0.5693	-0.1078	0.0675	0.0859*	
H503	0.4788	-0.0238	0.0988	0.0860*	
H501	0.5422	-0.1034	0.1504	0.0860*	
C51	0.6629 (6)	0.0941 (5)	0.0860 (3)	0.0701	
H513	0.6788	0.0447	0.0416	0.1057*	
H511	0.7264	0.1456	0.1074	0.1056*	
H512	0.5955	0.1334	0.0729	0.1060*	
C52	0.7501 (4)	-0.0316 (4)	0.1625 (4)	0.0744	
H523	0.7668	-0.0797	0.1169	0.1088*	
H522	0.8133	0.0216	0.1841	0.1088*	
H521	0.7365	-0.0768	0.1986	0.1091*	
H461	0.4721	0.0365	0.2282	0.0291*	
C53	0.2629 (3)	0.5158 (3)	0.7616 (2)	0.0238	
C54	0.3075 (3)	0.4378 (3)	0.8029 (2)	0.0253	
C55	0.3641 (3)	0.3540 (3)	0.7647 (2)	0.0227	
H551	0.3940	0.2984	0.7891	0.0272*	
C56	0.2923 (3)	0.4486 (3)	0.8856 (2)	0.0287	
C57	0.3511 (4)	0.3573 (4)	0.9216 (2)	0.0409	
H572	0.3399	0.3677	0.9735	0.0607*	
H573	0.3190	0.2859	0.8941	0.0609*	
H571	0.4311	0.3612	0.9199	0.0607*	
C58	0.1658 (4)	0.4404 (4)	0.8892 (2)	0.0353	
H581	0.1550	0.4490	0.9410	0.0526*	
H582	0.1332	0.3695	0.8605	0.0531*	
H583	0.1272	0.4973	0.8678	0.0529*	
C59	0.3450 (4)	0.5607 (3)	0.9314 (2)	0.0383	
H592	0.3406	0.5670	0.9842	0.0568*	
H593	0.3060	0.6205	0.9135	0.0570*	
H591	0.4239	0.5668	0.9264	0.0568*	
H531	0.2205	0.5718	0.7845	0.0283*	

K60	0.0000	0.0000	0.5000	0.0298	
O61	0.0353 (2)	0.0489 (2)	0.65806 (16)	0.0297	
C62	-0.0357 (5)	-0.0241 (5)	0.6878 (4)	0.0229	0.559 (8)
C63	0.0532 (9)	-0.0366 (7)	0.6937 (6)	0.0390	0.441 (8)
C64	-0.0232 (4)	-0.1362 (3)	0.6550 (3)	0.0367	
O65	-0.0695 (6)	-0.1655 (4)	0.5770 (3)	0.0228	0.559 (8)
O66	-0.0140 (8)	-0.1668 (6)	0.5810 (5)	0.0321	0.441 (8)
C67	-0.0868 (9)	-0.2625 (11)	0.5428 (9)	0.0338	0.441 (8)
C68	-0.0457 (8)	-0.2738 (7)	0.5394 (5)	0.0215	0.559 (8)
C69	0.1052 (7)	0.2889 (7)	0.5398 (6)	0.0231	0.559 (8)
C70	0.0625 (10)	0.2971 (10)	0.5367 (9)	0.0305	0.441 (8)
O71	0.1012 (8)	0.2130 (7)	0.5750 (5)	0.0342	0.441 (8)
O72	0.0497 (5)	0.2183 (5)	0.5783 (3)	0.0236	0.559 (8)
C73	0.0970 (4)	0.2298 (3)	0.6531 (2)	0.0368	
C74	0.0339 (5)	0.1586 (5)	0.6917 (3)	0.0226	0.559 (8)
C75	0.1171 (8)	0.1450 (7)	0.6886 (6)	0.0330	0.441 (8)
O76	0.3831 (4)	0.4796 (4)	0.1470 (3)	0.0676	
C77	0.4291 (4)	0.4068 (4)	0.1946 (3)	0.0489	
O78	0.2281 (3)	0.0004 (3)	0.4971 (3)	0.0590	
C79	0.3124 (6)	-0.0739 (5)	0.4994 (5)	0.0803	
H671	-0.0719	-0.3227	0.5697	0.0401*	0.441 (8)
H672	-0.1653	-0.2441	0.5412	0.0400*	0.441 (8)
H681	0.0350	-0.2800	0.5401	0.0260*	0.559 (8)
H682	-0.0735	-0.3296	0.5636	0.0261*	0.559 (8)
H692	0.1018	0.3656	0.5654	0.0281*	0.559 (8)
H691	0.1833	0.2699	0.5404	0.0277*	0.559 (8)
H701	-0.0181	0.3046	0.5355	0.0369*	0.441 (8)
H702	0.1019	0.3673	0.5618	0.0370*	0.441 (8)
H741	-0.0439	0.1807	0.6876	0.0270*	0.559 (8)
H742	0.0677	0.1692	0.7450	0.0268*	0.559 (8)
H751	0.1147	0.1706	0.7421	0.0400*	0.441 (8)
H752	0.1925	0.1210	0.6825	0.0400*	0.441 (8)
H732	0.0193	0.2497	0.6576	0.0439*	0.441 (8)
H734	0.1484	0.2925	0.6794	0.0438*	0.441 (8)
H733	0.0998	0.3070	0.6791	0.0437*	0.559 (8)
H731	0.1741	0.2039	0.6554	0.0438*	0.559 (8)
H643	-0.0076	-0.1977	0.6806	0.0440*	0.441 (8)
H644	-0.1007	-0.1158	0.6570	0.0439*	0.441 (8)
H642	0.0579	-0.1492	0.6599	0.0439*	0.559 (8)
H641	-0.0588	-0.1842	0.6819	0.0436*	0.559 (8)

H631	0.1314	-0.0566	0.6938	0.0460*	0.441 (8)
H632	0.0404	-0.0136	0.7455	0.0458*	0.441 (8)
H621	-0.0126	-0.0133	0.7427	0.0278*	0.559 (8)
H622	-0.1146	-0.0063	0.6759	0.0277*	0.559 (8)
H791	0.3512	-0.0760	0.4569	0.1213*	
H793	0.2779	-0.1462	0.4967	0.1210*	
H792	0.3645	-0.0523	0.5464	0.1213*	
H773	0.3809	0.3993	0.2305	0.0734*	
H771	0.5029	0.4351	0.2217	0.0733*	
H772	0.4360	0.3306	0.1609	0.0714*	
H761	0.356 (6)	0.530 (5)	0.176 (4)	0.1016*	
H431	0.0955	0.2742	0.0092	0.0549*	
H432	0.0838	0.3678	0.0801	0.0550*	
H433	0.2032	0.3212	0.0690	0.0550*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0156 (2)	0.0107 (2)	0.0249 (2)	-0.00129 (16)	0.00273 (18)	0.00788 (17)
F2	0.0136 (11)	0.0119 (11)	0.0250 (13)	-0.0024 (9)	0.0031 (10)	0.0080 (10)
Mn3	0.0152 (2)	0.0111 (2)	0.0264 (2)	-0.00116 (16)	0.00304 (18)	0.00823 (18)
O4	0.0171 (10)	0.0166 (10)	0.0274 (12)	-0.0015 (8)	0.0010 (9)	0.0124 (9)
C5	0.0196 (14)	0.0118 (13)	0.0253 (16)	0.0003 (11)	0.0047 (12)	0.0073 (11)
C6	0.0184 (14)	0.0142 (13)	0.0258 (16)	-0.0015 (11)	0.0025 (12)	0.0076 (12)
S7	0.0194 (4)	0.0131 (3)	0.0266 (4)	-0.0023 (3)	0.0034 (3)	0.0097 (3)
O8	0.0228 (11)	0.0115 (10)	0.0279 (12)	-0.0026 (8)	0.0032 (9)	0.0092 (9)
O9	0.0254 (12)	0.0159 (11)	0.0309 (13)	-0.0036 (9)	0.0044 (10)	0.0117 (9)
C10	0.0236 (16)	0.0159 (14)	0.0273 (17)	-0.0029 (12)	0.0030 (13)	0.0087 (12)
C11	0.0166 (14)	0.0145 (13)	0.0256 (16)	-0.0032 (11)	0.0038 (12)	0.0087 (12)
O12	0.0215 (11)	0.0136 (10)	0.0280 (12)	0.0009 (8)	0.0076 (9)	0.0107 (9)
C13	0.0211 (15)	0.0150 (14)	0.0285 (17)	-0.0041 (11)	0.0042 (13)	0.0079 (12)
S14	0.0168 (3)	0.0131 (3)	0.0281 (4)	-0.0026 (3)	0.0046 (3)	0.0058 (3)
O15	0.0178 (11)	0.0167 (10)	0.0312 (13)	-0.0020 (8)	0.0027 (9)	0.0062 (9)
O16	0.0187 (11)	0.0191 (11)	0.0331 (13)	-0.0018 (9)	0.0067 (10)	0.0052 (10)
C17	0.0193 (14)	0.0114 (13)	0.0267 (16)	-0.0008 (11)	-0.0003 (12)	0.0066 (12)
C18	0.0189 (14)	0.0118 (13)	0.0251 (16)	0.0004 (11)	0.0024 (12)	0.0093 (11)
O19	0.0200 (11)	0.0117 (10)	0.0301 (12)	-0.0022 (8)	0.0061 (9)	0.0053 (9)
C20	0.0189 (14)	0.0139 (13)	0.0294 (17)	-0.0010 (11)	0.0011 (12)	0.0117 (12)
S21	0.0170 (3)	0.0109 (3)	0.0277 (4)	-0.0021 (3)	0.0025 (3)	0.0065 (3)
O22	0.0195 (11)	0.0113 (9)	0.0291 (12)	-0.0018 (8)	0.0026 (9)	0.0102 (9)
O23	0.0227 (11)	0.0107 (10)	0.0332 (13)	-0.0039 (8)	0.0034 (10)	0.0041 (9)
C24	0.0162 (14)	0.0142 (13)	0.0289 (17)	-0.0029 (11)	0.0009 (12)	0.0079 (12)
C25	0.0232 (16)	0.0146 (14)	0.0284 (17)	-0.0046 (12)	0.0016 (13)	0.0071 (12)
C26	0.0253 (16)	0.0167 (14)	0.0290 (17)	-0.0050 (12)	0.0007 (13)	0.0077 (13)
C27	0.0201 (15)	0.0191 (15)	0.0297 (17)	-0.0034 (12)	-0.0011 (13)	0.0118 (13)
C28	0.0189 (14)	0.0139 (13)	0.0271 (16)	-0.0030 (11)	0.0022 (12)	0.0095 (12)
C29	0.0165 (14)	0.0124 (13)	0.0270 (16)	-0.0033 (10)	0.0036 (12)	0.0091 (12)
O30	0.0167 (10)	0.0126 (10)	0.0258 (12)	-0.0015 (8)	-0.0018 (9)	0.0043 (8)
S31	0.0162 (3)	0.0146 (3)	0.0282 (4)	-0.0005 (3)	0.0023 (3)	0.0105 (3)
C32	0.0206 (15)	0.0112 (13)	0.0267 (16)	-0.0002 (11)	0.0052 (12)	0.0067 (11)
C33	0.0214 (15)	0.0155 (14)	0.0260 (16)	0.0011 (11)	0.0010 (12)	0.0065 (12)
C34	0.0233 (16)	0.0203 (15)	0.0275 (17)	-0.0031 (12)	0.0013 (13)	0.0102 (13)
C35	0.0252 (16)	0.0170 (14)	0.0274 (17)	-0.0031 (12)	0.0029 (13)	0.0109 (13)
C36	0.0331 (19)	0.035 (2)	0.033 (2)	-0.0102 (16)	-0.0029 (15)	0.0187 (16)

C37	0.047 (3)	0.066 (3)	0.037 (2)	-0.027 (2)	-0.0111 (19)	0.034 (2)
C38	0.042 (2)	0.048 (2)	0.0277 (19)	-0.0159 (19)	-0.0019 (17)	0.0126 (18)
C39	0.043 (2)	0.037 (2)	0.056 (3)	-0.0016 (18)	-0.013 (2)	0.029 (2)
O40	0.0168 (10)	0.0193 (11)	0.0320 (13)	0.0012 (8)	0.0064 (9)	0.0115 (9)
O41	0.0181 (11)	0.0221 (11)	0.0340 (13)	0.0004 (9)	0.0013 (10)	0.0119 (10)
C42	0.0342 (19)	0.0210 (16)	0.0276 (18)	-0.0061 (14)	-0.0009 (14)	0.0081 (14)
C43	0.047 (2)	0.034 (2)	0.0291 (19)	-0.0109 (17)	-0.0012 (17)	0.0148 (16)
C44	0.041 (2)	0.055 (3)	0.035 (2)	-0.022 (2)	-0.0078 (18)	0.015 (2)
C45	0.070 (3)	0.034 (2)	0.033 (2)	0.009 (2)	-0.007 (2)	0.0015 (18)
C46	0.0243 (16)	0.0166 (14)	0.0314 (18)	-0.0049 (12)	0.0054 (13)	0.0055 (13)
C47	0.0271 (17)	0.0216 (16)	0.0316 (18)	-0.0056 (13)	0.0068 (14)	0.0045 (14)
C48	0.0229 (15)	0.0185 (15)	0.0250 (16)	-0.0047 (12)	0.0048 (13)	0.0062 (12)
C49	0.050 (3)	0.038 (2)	0.043 (2)	-0.024 (2)	0.023 (2)	-0.0127 (19)
C50	0.066 (3)	0.042 (3)	0.059 (3)	-0.023 (2)	0.035 (3)	-0.020 (2)
C51	0.108 (5)	0.053 (3)	0.049 (3)	-0.039 (3)	0.045 (3)	-0.015 (2)
C52	0.052 (3)	0.042 (3)	0.122 (6)	-0.009 (2)	0.043 (4)	-0.023 (3)
C53	0.0243 (16)	0.0161 (14)	0.0323 (18)	-0.0024 (12)	0.0074 (13)	0.0057 (13)
C54	0.0279 (17)	0.0191 (15)	0.0304 (18)	-0.0062 (13)	0.0060 (14)	0.0081 (13)
C55	0.0246 (16)	0.0169 (14)	0.0293 (17)	-0.0045 (12)	0.0045 (13)	0.0110 (13)
C56	0.036 (2)	0.0231 (17)	0.0283 (18)	-0.0049 (14)	0.0080 (15)	0.0069 (14)
C57	0.058 (3)	0.037 (2)	0.030 (2)	0.006 (2)	0.0091 (19)	0.0127 (17)
C58	0.039 (2)	0.039 (2)	0.030 (2)	-0.0069 (17)	0.0095 (16)	0.0087 (16)
C59	0.049 (2)	0.032 (2)	0.032 (2)	-0.0112 (18)	0.0087 (18)	0.0014 (16)
K60	0.0359 (6)	0.0169 (5)	0.0383 (6)	-0.0022 (4)	0.0085 (5)	0.0084 (4)
O61	0.0286 (13)	0.0217 (12)	0.0410 (15)	-0.0020 (10)	0.0111 (11)	0.0075 (11)
C62	0.020 (3)	0.023 (3)	0.030 (3)	0.001 (2)	0.009 (2)	0.011 (2)
C63	0.052 (7)	0.025 (4)	0.046 (6)	-0.002 (4)	0.023 (5)	0.010 (4)
C64	0.039 (2)	0.0289 (19)	0.046 (2)	-0.0085 (16)	0.0123 (18)	0.0142 (17)
O65	0.026 (3)	0.017 (2)	0.026 (2)	-0.004 (2)	0.004 (2)	0.0064 (17)
O66	0.031 (4)	0.018 (3)	0.051 (4)	-0.010 (3)	0.018 (4)	0.007 (3)
C67	0.009 (5)	0.017 (5)	0.078 (8)	-0.001 (4)	0.003 (6)	0.021 (5)
C68	0.017 (4)	0.013 (3)	0.036 (4)	0.001 (3)	0.005 (4)	0.009 (2)
C69	0.015 (4)	0.016 (3)	0.043 (4)	-0.003 (3)	0.014 (4)	0.008 (3)
C70	0.013 (5)	0.012 (4)	0.070 (7)	0.005 (4)	0.019 (6)	0.004 (4)
O71	0.037 (5)	0.019 (3)	0.050 (4)	-0.001 (4)	0.012 (4)	0.011 (3)
O72	0.025 (3)	0.014 (2)	0.032 (3)	-0.008 (2)	0.003 (3)	0.0096 (18)
C73	0.038 (2)	0.0285 (19)	0.041 (2)	-0.0137 (16)	0.0066 (18)	0.0007 (16)
C74	0.027 (3)	0.016 (3)	0.023 (3)	0.004 (2)	0.003 (2)	0.002 (2)
C75	0.032 (5)	0.021 (4)	0.047 (5)	-0.003 (3)	0.014 (4)	0.004 (4)
O76	0.071 (3)	0.056 (2)	0.073 (3)	0.005 (2)	0.009 (2)	0.010 (2)

C77	0.035 (2)	0.045 (3)	0.072 (3)	-0.0073 (19)	0.011 (2)	0.022 (2)
O78	0.0399 (18)	0.0345 (17)	0.109 (3)	0.0090 (14)	0.016 (2)	0.0267 (19)
C79	0.070 (4)	0.046 (3)	0.132 (7)	0.026 (3)	0.024 (4)	0.030 (4)

Geometric parameters (Å, º) for (1)

Mn1—Mn3^{i}	3.1189 (7)	C45—H453	0.969
Mn1—F2	2.2091 (4)	C46—C47	1.381 (5)
Mn1—Mn3	3.1057 (7)	C46—H461	0.932
Mn1—O4	2.239 (2)	C47—C48	1.391 (4)
Mn1—O8	2.191 (2)	C47—C49	1.540 (5)
Mn1—O12	2.212 (2)	C48—H481	0.931
Mn1—O19	2.223 (2)	C49—C50	1.513 (6)
Mn1—O22	2.189 (2)	C49—C51	1.506 (7)
Mn1—O30	2.221 (2)	C49—C52	1.5045 (19)
F2—Mn3^{i}	2.1924 (5)	C50—H502	0.971
F2—Mn3	2.1924 (5)	C50—H503	0.982
Mn3—O4^{i}	2.242 (2)	C50—H501	0.972
Mn3—O19^{i}	2.247 (2)	C51—H513	0.961
Mn3—O12	2.225 (2)	C51—H511	0.962
Mn3—O15	2.177 (2)	C51—H512	0.969
Mn3—O30	2.222 (2)	C52—H523	0.974
Mn3—O40	2.188 (2)	C52—H522	0.973
O4—C5	1.305 (4)	C52—H521	0.975
C5—C6	1.425 (4)	C53—C54	1.394 (5)
C5—C32	1.430 (4)	C53—H531	0.936
C6—S7	1.763 (3)	C54—C55	1.380 (5)
C6—C35	1.389 (4)	C54—C56	1.532 (5)
S7—O8	1.446 (2)	C55—H551	0.935
S7—O9	1.439 (2)	C56—C57	1.534 (5)
S7—C10	1.769 (3)	C56—C58	1.535 (5)
C10—C11	1.432 (4)	C56—C59	1.532 (5)
C10—C55	1.394 (5)	C57—H572	0.964
C11—O12	1.297 (4)	C57—H573	0.962
C11—C13	1.429 (5)	C57—H571	0.967
C13—S14	1.762 (3)	C58—H581	0.962
C13—C53	1.386 (5)	C58—H582	0.964
S14—C17^{i}	1.763 (3)	C58—H583	0.957
S14—O15	1.445 (3)	C59—H592	0.963
S14—O16	1.436 (2)	C59—H593	0.960
C17—C18	1.425 (4)	C59—H591	0.970
C17—C48	1.392 (5)	O61—C62	1.468 (6)
C18—O19	1.303 (4)	O61—C74	1.369 (6)
C18—C20	1.428 (4)	O61—C63	1.345 (10)
C20—S21	1.768 (3)	O61—C75	1.483 (9)

C20—C46	1.388 (5)	C62—C64	1.411 (7)
S21—O22	1.449 (2)	C62—H621	0.977
S21—O23	1.438 (2)	C62—H622	0.975
S21—C24	1.768 (3)	C63—C64	1.501 (10)
C24—C25	1.392 (5)	C63—H631	0.975
C24—C29	1.424 (4)	C63—H632	0.971
C25—C26	1.380 (5)	C64—O65	1.413 (7)
C25—H251	0.935	C64—H642	0.982
C26—C27	1.391 (5)	C64—H641	0.976
C26—C42	1.531 (5)	C64—O66	1.352 (9)
C27—C28	1.383 (5)	C64—H643	0.970
C27—H271	0.931	C64—H644	0.972
C28—C29	1.434 (4)	O65—C68	1.429 (10)
C28—S31	1.770 (3)	O66—C67	1.443 (15)
C29—O30	1.297 (4)	C67—C70^{ii}	1.51 (2)
S31—C32^{i}	1.768 (3)	C67—H671	0.971
S31—O40	1.442 (3)	C67—H672	0.970
S31—O41	1.439 (2)	C68—C69^{ii}	1.478 (14)
C32—C33	1.382 (4)	C68—H681	0.972
C33—C34	1.387 (4)	C68—H682	0.969
C33—H331	0.935	C69—O72	1.441 (10)
C34—C35	1.393 (5)	C69—H692	0.972
C34—C36	1.527 (5)	C69—H691	0.969
C35—H351	0.933	C70—O71	1.404 (15)
C36—C37	1.533 (5)	C70—H701	0.971
C36—C38	1.538 (6)	C70—H702	0.970
C36—C39	1.528 (6)	O71—C73	1.411 (10)
C37—H371	0.964	O72—C73	1.370 (7)
C37—H372	0.965	C73—C74	1.497 (7)
C37—H373	0.967	C73—H733	0.971
C38—H383	0.955	C73—H731	0.981
C38—H382	0.966	C73—C75	1.338 (10)
C38—H381	0.963	C73—H732	0.980
C39—H391	0.966	C73—H734	0.974
C39—H392	0.961	C74—H741	0.973
C39—H393	0.963	C74—H742	0.974
C42—C43	1.537 (5)	C75—H751	0.973
C42—C44	1.528 (6)	C75—H752	0.973
C42—C45	1.525 (6)	O76—C77	1.424 (6)
C43—H431	0.974	O76—H761	0.844 (19)

C43—H432	0.972	C77—H773	0.960
C43—H433	0.962	C77—H771	0.964
C44—H443	0.967	C77—H772	1.028
C44—H441	0.965	O78—C79	1.374 (6)
C44—H442	0.957	C79—H791	0.966
C45—H451	0.967	C79—H793	0.966
C45—H452	0.960	C79—H792	0.962
Mn3^{i}—Mn1—F2	44.663 (12)	C36—C39—H391	109.7
Mn3^{i}—Mn1—Mn3	89.565 (18)	C36—C39—H392	109.6
F2—Mn1—Mn3	44.902 (12)	H391—C39—H392	110.0
Mn3^{i}—Mn1—O4	45.93 (6)	C36—C39—H393	110.7
F2—Mn1—O4	74.29 (6)	H391—C39—H393	108.6
Mn3—Mn1—O4	108.26 (6)	H392—C39—H393	108.2
Mn3^{i}—Mn1—O8	125.99 (6)	Mn3—O40—S31	125.79 (14)
F2—Mn1—O8	144.00 (7)	C26—C42—C43	109.5 (3)
Mn3—Mn1—O8	124.10 (7)	C26—C42—C44	109.1 (3)
O4—Mn1—O8	81.56 (8)	C43—C42—C44	109.4 (3)
Mn3^{i}—Mn1—O12	108.94 (6)	C26—C42—C45	111.7 (3)
F2—Mn1—O12	74.85 (6)	C43—C42—C45	107.9 (4)
Mn3—Mn1—O12	45.75 (6)	C44—C42—C45	109.2 (4)
O4—Mn1—O12	92.26 (9)	C42—C43—H431	110.3
O8—Mn1—O12	79.93 (8)	C42—C43—H432	110.6
Mn3^{i}—Mn1—O19	46.08 (6)	H431—C43—H432	108.7
F2—Mn1—O19	74.32 (6)	C42—C43—H433	109.2
Mn3—Mn1—O19	108.19 (6)	H431—C43—H433	108.3
O4—Mn1—O19	80.37 (9)	H432—C43—H433	109.7
O8—Mn1—O19	127.66 (9)	C42—C44—H443	110.1
Mn3^{i}—Mn1—O22	126.51 (6)	C42—C44—H441	111.1
F2—Mn1—O22	144.37 (6)	H443—C44—H441	109.7
Mn3—Mn1—O22	123.98 (6)	C42—C44—H442	109.7
O4—Mn1—O22	127.73 (8)	H443—C44—H442	108.1
O8—Mn1—O22	71.58 (8)	H441—C44—H442	108.0
Mn3^{i}—Mn1—O30	109.20 (6)	C42—C45—H451	109.8
F2—Mn1—O30	74.98 (6)	C42—C45—H452	110.2
Mn3—Mn1—O30	45.66 (6)	H451—C45—H452	109.4
O4—Mn1—O30	149.25 (8)	C42—C45—H453	109.8
O8—Mn1—O30	124.64 (8)	H451—C45—H453	109.1
O12—Mn1—O19	149.16 (8)	H452—C45—H453	108.6
O12—Mn1—O22	124.41 (9)	C20—C46—C47	122.4 (3)

O19—Mn1—O22	81.97 (8)	C20—C46—H461	117.6
O12—Mn1—O30	78.71 (9)	C47—C46—H461	120.0
O19—Mn1—O30	92.40 (9)	C46—C47—C48	116.1 (3)
O22—Mn1—O30	79.93 (8)	C46—C47—C49	124.4 (3)
Mn3^{i}—F2—Mn1	90.241 (18)	C48—C47—C49	119.4 (3)
Mn3^{i}—F2—Mn1^{i}	89.759 (18)	C17—C48—C47	122.3 (3)
Mn1—F2—Mn1^{i}	179.995	C17—C48—H481	118.6
Mn3^{i}—F2—Mn3	179.995	C47—C48—H481	119.1
Mn1—F2—Mn3	89.759 (18)	C47—C49—C50	111.5 (3)
Mn1^{i}—F2—Mn3	90.241 (18)	C47—C49—C51	109.5 (4)
F2—Mn3—O4^{i}	74.56 (6)	C50—C49—C51	111.1 (4)
F2—Mn3—O19^{i}	74.17 (6)	C47—C49—C52	110.3 (4)
O4^{i}—Mn3—O19^{i}	79.80 (8)	C50—C49—C52	107.3 (4)
F2—Mn3—Mn1	45.339 (12)	C51—C49—C52	107.0 (5)
O4^{i}—Mn3—Mn1	108.88 (6)	C49—C50—H502	108.2
O19^{i}—Mn3—Mn1	108.63 (6)	C49—C50—H503	108.9
F2—Mn3—Mn1^{i}	45.096 (12)	H502—C50—H503	110.8
O4^{i}—Mn3—Mn1^{i}	45.86 (6)	C49—C50—H501	108.3
O19^{i}—Mn3—Mn1^{i}	45.44 (6)	H502—C50—H501	110.0
Mn1—Mn3—Mn1^{i}	90.435 (18)	H503—C50—H501	110.5
F2—Mn3—O12	74.92 (6)	C49—C51—H513	109.2
O4^{i}—Mn3—O12	149.47 (8)	C49—C51—H511	108.5
O19^{i}—Mn3—O12	92.82 (9)	H513—C51—H511	109.7
Mn1—Mn3—O12	45.41 (6)	C49—C51—H512	109.0
Mn1^{i}—Mn3—O12	109.47 (6)	H513—C51—H512	109.8
F2—Mn3—O15	143.93 (7)	H511—C51—H512	110.6
O4^{i}—Mn3—O15	127.23 (9)	C49—C52—H523	110.2
O19^{i}—Mn3—O15	81.68 (9)	C49—C52—H522	110.4
Mn1—Mn3—O15	123.85 (6)	H523—C52—H522	109.3
Mn1^{i}—Mn3—O15	125.57 (6)	C49—C52—H521	107.0
F2—Mn3—O30	75.29 (6)	H523—C52—H521	109.3
O4^{i}—Mn3—O30	92.95 (9)	H522—C52—H521	110.6
O19^{i}—Mn3—O30	149.45 (8)	C13—C53—C54	122.7 (3)
Mn1—Mn3—O30	45.64 (6)	C13—C53—H531	118.5
Mn1^{i}—Mn3—O30	109.84 (6)	C54—C53—H531	118.8
F2—Mn3—O40	144.31 (7)	C53—C54—C55	115.9 (3)
O4^{i}—Mn3—O40	81.61 (8)	C53—C54—C56	120.0 (3)
O19^{i}—Mn3—O40	127.42 (9)	C55—C54—C56	124.1 (3)
Mn1—Mn3—O40	123.92 (6)	C10—C55—C54	122.3 (3)
Mn1^{i}—Mn3—O40	125.88 (6)	C10—C55—H551	118.1

O12—Mn3—O15	80.03 (9)	C54—C55—H551	119.6
O12—Mn3—O30	78.41 (9)	C54—C56—C57	111.8 (3)
O15—Mn3—O30	124.46 (8)	C54—C56—C58	109.3 (3)
O12—Mn3—O40	124.52 (8)	C57—C56—C58	108.7 (3)
O15—Mn3—O40	71.73 (9)	C54—C56—C59	109.1 (3)
O30—Mn3—O40	79.88 (9)	C57—C56—C59	107.8 (3)
Mn1—O4—Mn3^{i}	88.21 (8)	C58—C56—C59	110.3 (3)
Mn1—O4—C5	136.11 (19)	C56—C57—H572	108.9
Mn3^{i}—O4—C5	135.5 (2)	C56—C57—H573	109.5
O4—C5—C6	123.5 (3)	H572—C57—H573	109.5
O4—C5—C32	123.9 (3)	C56—C57—H571	109.9
C6—C5—C32	112.7 (3)	H572—C57—H571	109.6
C5—C6—S7	122.2 (2)	H573—C57—H571	109.3
C5—C6—C35	123.2 (3)	C56—C58—H581	110.1
S7—C6—C35	114.4 (2)	C56—C58—H582	109.9
C6—S7—O8	110.02 (15)	H581—C58—H582	109.7
C6—S7—O9	107.85 (15)	C56—C58—H583	110.4
O8—S7—O9	116.36 (14)	H581—C58—H583	108.5
C6—S7—C10	105.07 (15)	H582—C58—H583	108.1
O8—S7—C10	109.71 (15)	C56—C59—H592	110.2
O9—S7—C10	107.20 (15)	C56—C59—H593	110.4
Mn1—O8—S7	125.28 (13)	H592—C59—H593	108.7
S7—C10—C11	123.1 (3)	C56—C59—H591	109.6
S7—C10—C55	113.4 (2)	H592—C59—H591	108.7
C11—C10—C55	123.5 (3)	H593—C59—H591	109.2
C10—C11—O12	124.0 (3)	C62—O61—C74	113.3 (4)
C10—C11—C13	112.2 (3)	C63—O61—C75	114.4 (6)
O12—C11—C13	123.8 (3)	O61—C62—C64	110.2 (4)
Mn1—O12—Mn3	88.84 (8)	O61—C62—H621	109.3
Mn1—O12—C11	135.2 (2)	C64—C62—H621	108.9
Mn3—O12—C11	134.7 (2)	O61—C62—H622	109.5
C11—C13—S14	123.5 (3)	C64—C62—H622	109.4
C11—C13—C53	123.2 (3)	H621—C62—H622	109.7
S14—C13—C53	113.2 (3)	O61—C63—C64	112.0 (8)
C17^{i}—S14—C13	105.20 (15)	O61—C63—H631	108.1
C17^{i}—S14—O15	109.58 (15)	C64—C63—H631	108.8
C13—S14—O15	109.64 (15)	O61—C63—H632	109.0
C17^{i}—S14—O16	107.34 (15)	C64—C63—H632	109.2
C13—S14—O16	107.57 (15)	H631—C63—H632	109.6
O15—S14—O16	116.86 (15)	C62—C64—O65	113.8 (5)

Mn3—O15—S14	125.86 (14)	C62—C64—H642	108.1
S14^{i}—C17—C18	122.8 (2)	O65—C64—H642	107.1
S14^{i}—C17—C48	113.9 (2)	C62—C64—H641	109.5
C18—C17—C48	123.2 (3)	O65—C64—H641	108.8
C17—C18—O19	123.7 (3)	H642—C64—H641	109.3
C17—C18—C20	112.5 (3)	C63—C64—O66	111.3 (6)
O19—C18—C20	123.9 (3)	C63—C64—H643	110.8
Mn1—O19—Mn3^{i}	88.47 (9)	O66—C64—H643	110.4
Mn1—O19—C18	135.98 (19)	C63—C64—H644	107.9
Mn3^{i}—O19—C18	135.3 (2)	O66—C64—H644	107.4
C18—C20—S21	122.0 (3)	H643—C64—H644	108.8
C18—C20—C46	123.5 (3)	C64—O65—C68	115.5 (6)
S21—C20—C46	114.3 (2)	C64—O66—C67	112.2 (8)
C20—S21—O22	109.83 (15)	C70^{ii}—C67—O66	108.4 (10)
C20—S21—O23	107.95 (15)	C70^{ii}—C67—H671	109.7
O22—S21—O23	116.47 (14)	O66—C67—H671	109.7
C20—S21—C24	105.27 (14)	C70^{ii}—C67—H672	109.9
O22—S21—C24	109.53 (15)	O66—C67—H672	110.0
O23—S21—C24	107.18 (15)	H671—C67—H672	109.2
Mn1—O22—S21	125.22 (12)	C69^{ii}—C68—O65	106.6 (7)
S21—C24—C25	113.5 (2)	C69^{ii}—C68—H681	109.6
S21—C24—C29	123.2 (2)	O65—C68—H681	110.7
C25—C24—C29	123.3 (3)	C69^{ii}—C68—H682	110.0
C24—C25—C26	123.0 (3)	O65—C68—H682	110.2
C24—C25—H251	117.9	H681—C68—H682	109.8
C26—C25—H251	119.1	C68^{ii}—C69—O72	109.0 (7)
C25—C26—C27	115.3 (3)	C68^{ii}—C69—H692	109.5
C25—C26—C42	124.1 (3)	O72—C69—H692	108.7
C27—C26—C42	120.6 (3)	C68^{ii}—C69—H691	109.7
C26—C27—C28	122.9 (3)	O72—C69—H691	110.1
C26—C27—H271	118.1	H692—C69—H691	109.8
C28—C27—H271	119.0	C67^{ii}—C70—O71	106.3 (10)
C27—C28—C29	123.3 (3)	C67^{ii}—C70—H701	110.1
C27—C28—S31	113.3 (2)	O71—C70—H701	110.5
C29—C28—S31	123.4 (3)	C67^{ii}—C70—H702	110.7
C28—C29—C24	112.1 (3)	O71—C70—H702	110.2
C28—C29—O30	123.5 (3)	H701—C70—H702	109.0
C24—C29—O30	124.3 (3)	C70—O71—C73	117.6 (9)
Mn1—O30—Mn3	88.70 (8)	C69—O72—C73	112.9 (6)
Mn1—O30—C29	134.8 (2)	O72—C73—C74	111.2 (4)

Mn3—O30—C29	135.40 (19)	O72—C73—H733	110.7
C28—S31—C32^{i}	105.11 (15)	C74—C73—H733	110.5
C28—S31—O40	109.67 (15)	O72—C73—H731	107.7
C32^{i}—S31—O40	109.66 (15)	C74—C73—H731	107.2
C28—S31—O41	107.56 (15)	H733—C73—H731	109.4
C32^{i}—S31—O41	107.07 (15)	O71—C73—C75	118.8 (6)
O40—S31—O41	117.08 (15)	O71—C73—H732	105.4
C5—C32—S31^{i}	122.5 (2)	C75—C73—H732	105.9
C5—C32—C33	123.2 (3)	O71—C73—H734	108.4
S31^{i}—C32—C33	114.2 (2)	C75—C73—H734	109.0
C32—C33—C34	122.9 (3)	H732—C73—H734	109.0
C32—C33—H331	118.6	C73—C74—O61	110.8 (5)
C34—C33—H331	118.5	C73—C74—H741	108.3
C33—C34—C35	115.6 (3)	O61—C74—H741	109.2
C33—C34—C36	120.6 (3)	C73—C74—H742	109.9
C35—C34—C36	123.8 (3)	O61—C74—H742	109.5
C34—C35—C6	122.5 (3)	H741—C74—H742	109.1
C34—C35—H351	119.1	O61—C75—C73	113.5 (7)
C6—C35—H351	118.3	O61—C75—H751	108.8
C34—C36—C37	111.4 (3)	C73—C75—H751	108.9
C34—C36—C38	109.2 (3)	O61—C75—H752	108.5
C37—C36—C38	108.4 (4)	C73—C75—H752	107.6
C34—C36—C39	109.3 (3)	H751—C75—H752	109.5
C37—C36—C39	108.9 (4)	C77—O76—H761	104 (6)
C38—C36—C39	109.6 (3)	O76—C77—H773	110.7
C36—C37—H371	109.2	O76—C77—H771	110.1
C36—C37—H372	109.7	H773—C77—H771	109.1
H371—C37—H372	109.2	O76—C77—H772	108.1
C36—C37—H373	110.9	H773—C77—H772	109.5
H371—C37—H373	109.7	H771—C77—H772	109.4
H372—C37—H373	108.2	O78—C79—H791	110.2
C36—C38—H383	110.8	O78—C79—H793	107.9
C36—C38—H382	109.6	H791—C79—H793	109.6
H383—C38—H382	108.2	O78—C79—H792	109.2
C36—C38—H381	109.9	H791—C79—H792	110.5
H383—C38—H381	109.0	H793—C79—H792	109.5
H382—C38—H381	109.3		

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+1; (ii) -*x*, -*y*, -*z*+1.

Hydrogen-bond geometry (Å, º) for (1)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C52—H522···C63^{iii}	0.97	2.50	3.195 (7)	129 (1)
C68—H681···O15^{iv}	0.97	2.54	3.365 (7)	142 (1)
C70—H701···O40^{v}	0.97	2.58	3.394 (7)	141 (1)
C73—H733···O41^{v}	0.97	2.46	3.249 (7)	138 (1)
C64—H643···O16^{iv}	0.97	2.40	3.207 (7)	140 (1)

Symmetry codes: (iii) -*x*+1, -*y*, -*z*+1; (iv) *x*, *y*-1, *z*; (v) -*x*, -*y*+1, -*z*+1.

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Photophysical characterisations

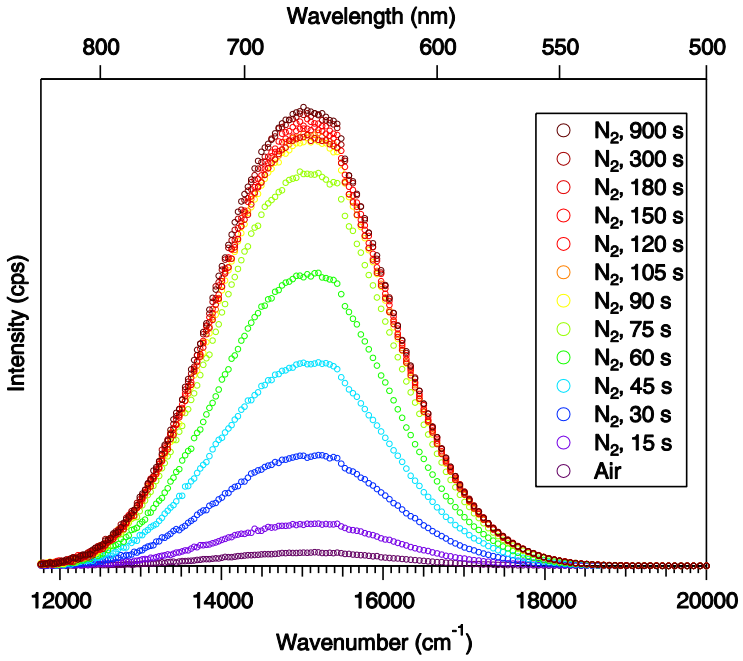

Fig. S1 Solution emission spectra of $[Mn_4(ThiaSO_2)_2F]K$ **1** after different times (0 – 900 s) of de-oxygenation by N_2 bubbling and upon photoexcitation at 28570 cm^{-1} (350 nm).

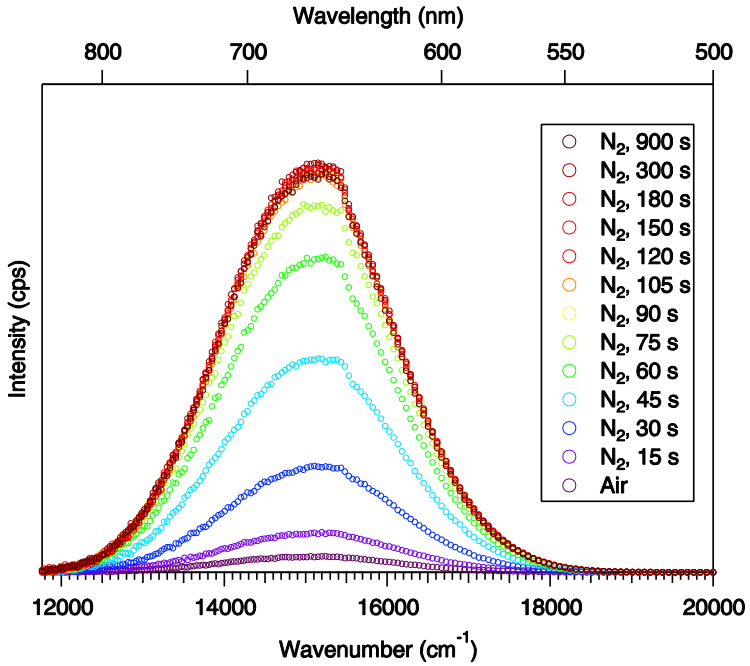

Fig. S2 Solution emission spectra of $[Mn_4(ThiaSO_2)_2F][K(18C6)]$ **2** after different times (0 – 900 s) of de-oxygenation by N_2 bubbling and upon photoexcitation at 28570 cm^{-1} (350 nm).

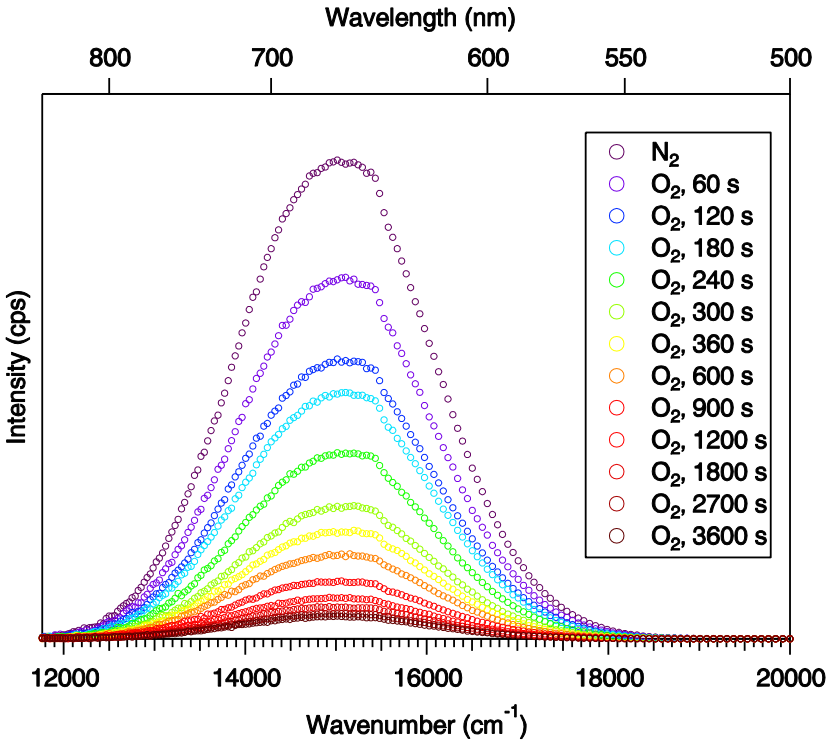

Fig. S3 Solution emission spectra of $[Mn_4(ThiaSO_2)_2F]K$ **1** as function of time (0 – 3600 s) of re-oxygenation of the N_2 saturated solution by exposing them to air and upon photoexcitation at 28570 cm^{-1} (350 nm).

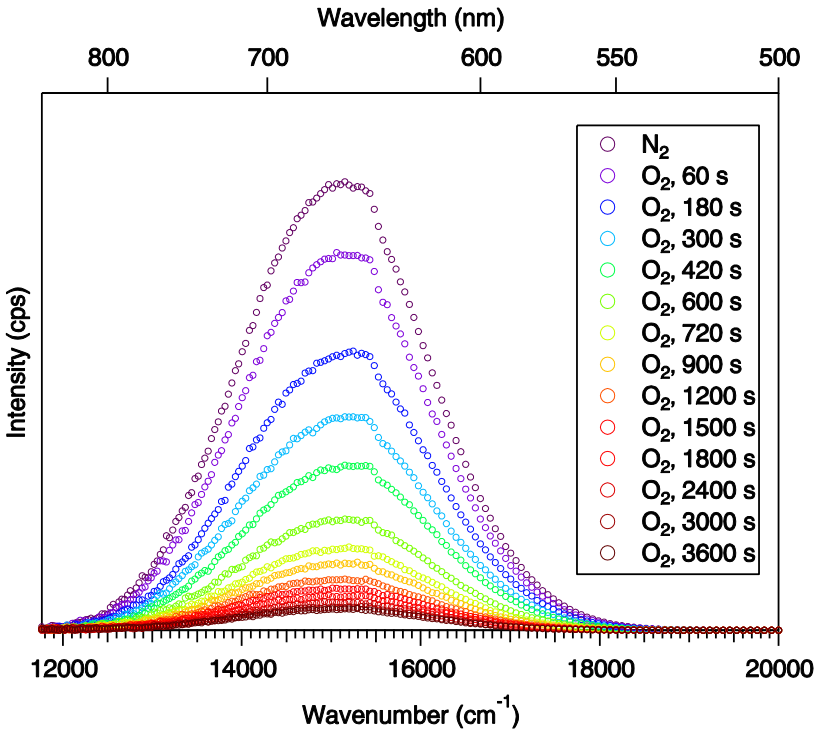

Fig. S4 Solution emission spectra of $[Mn_4(ThiaSO_2)_2F][K(18C6)]$ **2** as function of time (0 – 3600 s) of re-oxygenation of the N_2 saturated solution by exposing them to air and upon photoexcitation at 28570 cm^{-1} (350 nm).

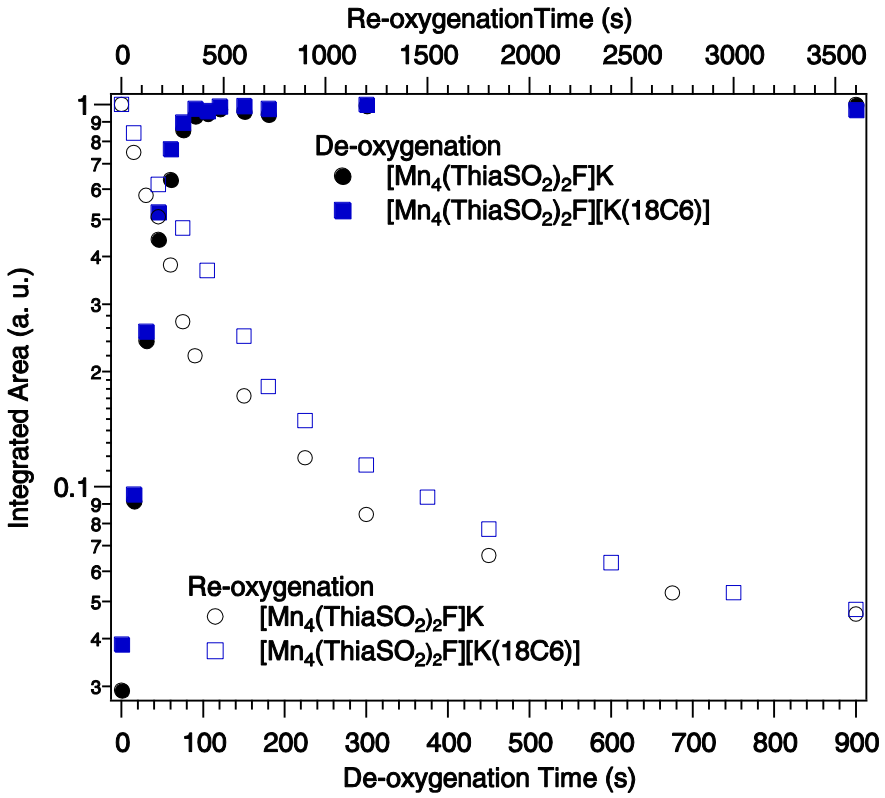

Fig. S5 Integrated solution luminescence intensities of $[Mn_4(ThiaSO_2)_2F]K$ **1** (black circles) and $[Mn_4(ThiaSO_2)_2F][K(18C6)]$ **2** (blue squares) after different times of de-oxygenation by N_2 bubbling (0 – 900 s, bottom axis) and re-oxygenation of the N_2 saturated solution by exposing them to air (0 – 3600 s, top axis) upon photoexcitation at 28570 cm^{-1} (350 nm).