Electronic Supporting Information

Achievement of ligand-field induced thermochromic luminescence via two-step single-crystal to single-crystal transformations

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Table S1. Crystallographic Data of complex **1** at various temperatures.

temperature	480 K	440 K	420 K	410 K	400 K	390 K	360 K
formula	$C_{29}H_{23}Br_2MnNO_2P_2$	$C_{29}H_{23}Br_2MnNO_2P_2$	$C_{29}H_{23}Br_2MnNO_2P_2$	$C_{29}H_{23}Br_2MnNO_2P_2$	$C_{29}H_{23}Br_2MnNO_2P_2$	$C_{29}H_{23}Br_2MnNO_2P_2$	$C_{29}H_{23}Br_2MnNO_2P_2$
formula weight	694.18	694.18	694.18	694.18	694.18	694.18	694.18
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / Å	10.449(3)	10.4536(9)	10.4487(14)	10.4868(12)	10.4577(17)	12.3470(10)	12.352(10)
b / Å	12.532(3)	12.5100(10)	12.5208(16)	12.5077(14)	12.4576(19)	15.1937(12)	15.347(11)
c / Å	12.846(3)	12.7069(10)	12.6339(16)	12.6045(13)	12.4979(18)	17.2550(15)	17.295(12)
α / deg	84.230(8)	84.743(3)	84.869(5)	85.095(4)	85.451(5)	100.149(3)	99.95(2)
β / deg	67.331(7)	67.952(3)	68.184(5)	68.271(4)	68.607(5)	105.447(3)	104.61(2)
γ / deg	81.688(8)	82.162(3)	82.196(5)	82.281(4)	82.521(6)	100.713(3)	100.46(2)
volume / Å^3	1534.0(6)	1524.3(2)	1518.9(3)	1520.7(3)	1502.2(4)	2977.3(4)	3036(4)
Z	2	2	2	2	2	4	4
ρ_{calc} / g.cm^{-3}	1.503	1.512	1.518	1.516	1.535	1.550	1.519
μ / mm^{-1}	3.165	3.185	3.196	3.192	3.232	3.261	3.198
radiation(λ) / Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
R_1	0.0523	0.0575	0.0597	0.0854	0.0585	0.0510	0.0592
wR_2	0.1481	0.1628	0.1797	0.1856	0.1435	0.1377	0.1365
GOF	0.904	1.109	1.060	1.026	1.017	1.015	0.900

temperature	320 K	300 K	260 K	200 K	140 K	80 K
formula	$C_{29}H_{23}Br_2MnNO_2P_2$	$C_{29}H_{23}Br_2MnNO_2P_2$	$C_{29}H_{23}Br_2MnNO_2P_2$	$C_{29}H_{23}Br_2MnNO_2P_2$	$C_{29}H_{23}Br_2MnNO_2P_2$	$C_{29}H_{23}Br_2MnNO_2P_2$
formula weight	694.18	694.18	694.18	694.18	694.18	694.18
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / Å	12.089(2)	13.0769(4)	13.1370(12)	13.182(2)	13.2006(8)	13.2012(9)
b / Å	15.242(3)	15.2036(4)	15.1638(11)	15.175(3)	15.1682(8)	15.1666(10)
c / Å	17.019(4)	16.9342(5)	16.7360(12)	16.539(3)	16.4695(9)	16.3854(11)
α / deg	100.060(7)	99.7454(10)	99.164(3)	98.923(6)	98.582(2)	98.384(2)
β / deg	104.032(7)	109.6649(10)	110.439(3)	110.826(6)	111.110(2)	111.380(2)
γ / deg	100.712(7)	107.5342(9)	107.866(3)	108.110(6)	108.380(2)	108.519(2)
volume / Å^3	2908.8(10)	2882.51(15)	2837.6(4)	2804.4(8)	2787.8(3)	2766.6(3)
Z	4	4	4	4	4	4
ρ_{calc} / g.cm^{-3}	1.585	1.600	1.625	1.644	1.654	1.667
μ / mm^{-1}	3.338	3.368	3.421	3.462	3.483	3.509
radiation(λ) / Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
R_1	0.0358	0.0777	0.0645	0.0302	0.0267	0.0263
wR_2	0.1131	0.2031	0.1683	0.0726	0.0671	0.0533
GOF	1.120	1.074	1.001	1.094	1.037	1.016

Table S2. Selected interatomic distances (Å) and angles (°) of complex **1** at various temperatures.

temp. (K)	Mn–Br[a]	Mn···Mn[b]	O-Mn-Br[c]
480	4.766(2)	5.708(2)	173.0(1)
440	4.652(1)	5.548(1)	171.4(1)
420	4.600(1)	5.473(1)	170.2(1)
410	4.568(2)	5.430(2)	169.9(2)
400	4.496(1)	5.332(1)	169.5(1)
390	4.191(1)	5.031(1)	168.0(1)
	4.588(1)	5.350(1)	168.4(1)
360	4.043(3)	4.883(3)	167.2(1)
	4.515(3)	5.273(3)	167.9(1)
320	3.749(1)	4.592(1)	167.16(7)
	4.280(1)	5.039(1)	167.59(7)
300	3.739(2)	4.583(2)	167.6(2)
	3.754(3)	4.558(3)	168.1(2)
260	3.432(1)	4.340(1)	166.8(1)
	3.490(1)		168.4(1)
200	3.1946(8)	4.1187(9)	167.40(6)
	3.2221(8)		168.48(6)
140	3.0757(7)	4.0084(6)	167.73(6)
	3.0918(7)		168.62(6)
80	2.9962(5)	3.9292(5)	167.83(5)
	3.0042(5)		168.41(5)

[a] The shortest Mn–Br distances between adjacent manganese(II) coordination chains. [b] The shortest Mn···Mn distances between adjacent coordination chains. [c] The axial O-Mn-Br angles in trigonal bipyramidal geometry.

Table S3. The Emission Wavelengths, Luminescent Lifetimes and CIE Chromatic Coordinates of Manganese(II) Complex **1** at various temperatures in the range of 480–80 K.

temp (K)	80	100	140	180	220	260	280	300	320
λ_{em} (nm)	617	615	612	609	604	599	595	588	585
τ_{em} (μs)	2097	2077	2020	1894	1738	1311	949	658	266 37.3
CIE coordinate	0.6508 0.3483	0.6450 0.3542	0.6302 0.3690	0.6115 0.3876	0.5888 0.4101	0.5641 0.4342	0.5504 0.4474	0.5341 0.4631	0.5157 0.4786
temp (K)	340	360	380	390	400	410	420	440	480
λ_{em} (nm)	584	581	581	580	517 592	514 596	508 612	506 615	502
τ_{em} (μs)	231 27.3	97.9 8.3	79.4 5.8	68.3 4.7	46.4 4.1	48.7 3.9	57.1 3.4	67.4 3.2	78.5 2.7
CIE coordinate	0.5077 0.4820	0.4922 0.4886	0.4685 0.4965	0.4557 0.4985	0.4406 0.4999	0.4303 0.4953	0.4106 0.4970	0.3237 0.5285	0.1959 0.5631

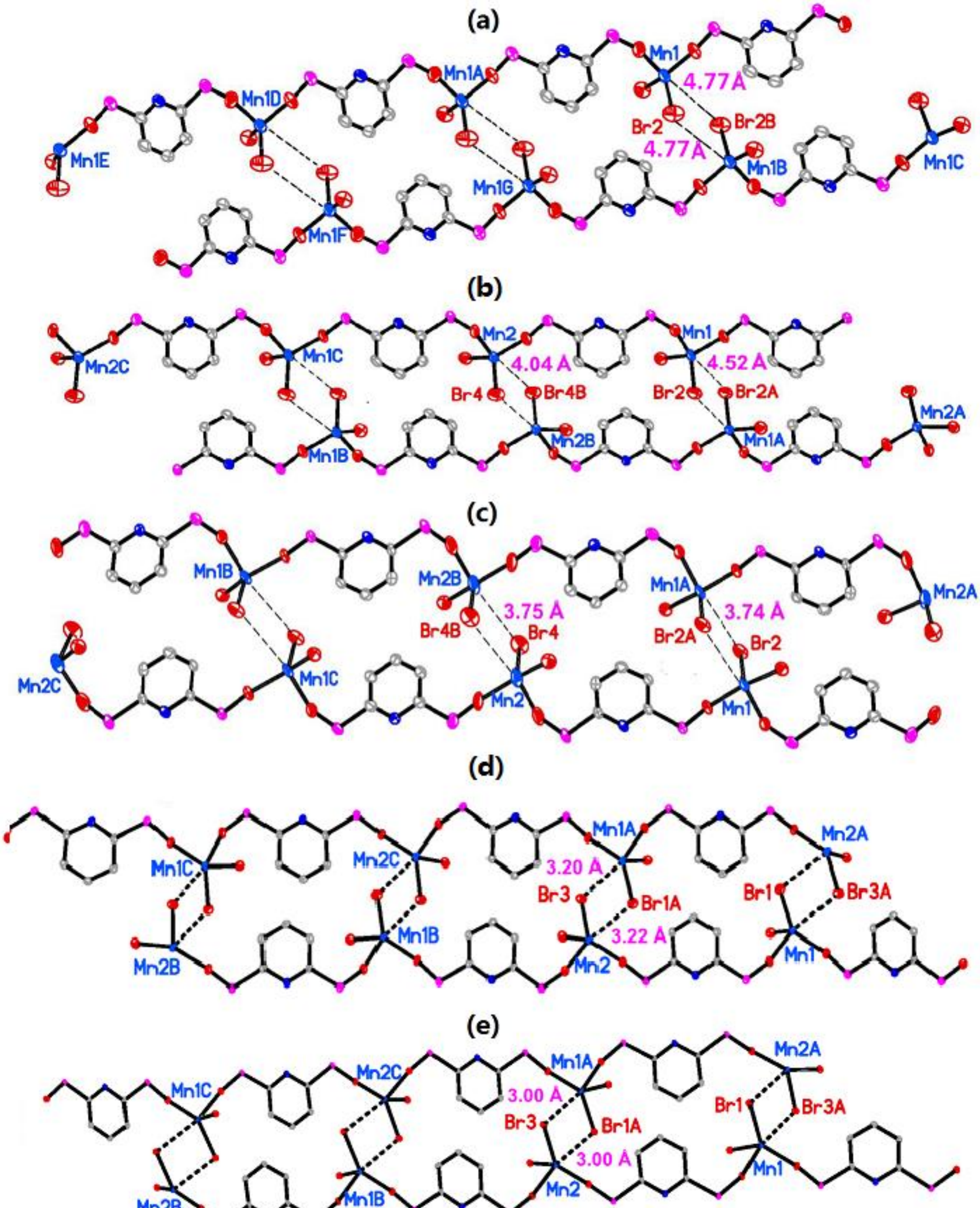


Fig. S1 The perspective views of one-dimensional manganese(II) complex **1** (30% thermal ellipsoids) at 480 K (a), 360 K (b), 300 K (c), 200 K (d), and 80 K (e), showing gradually reduced Mn−Br distances between two adjacent chains so as to produce interchain Mn−Br linkages. Phenyl rings on the phosphorus atoms are omitted for clarity.

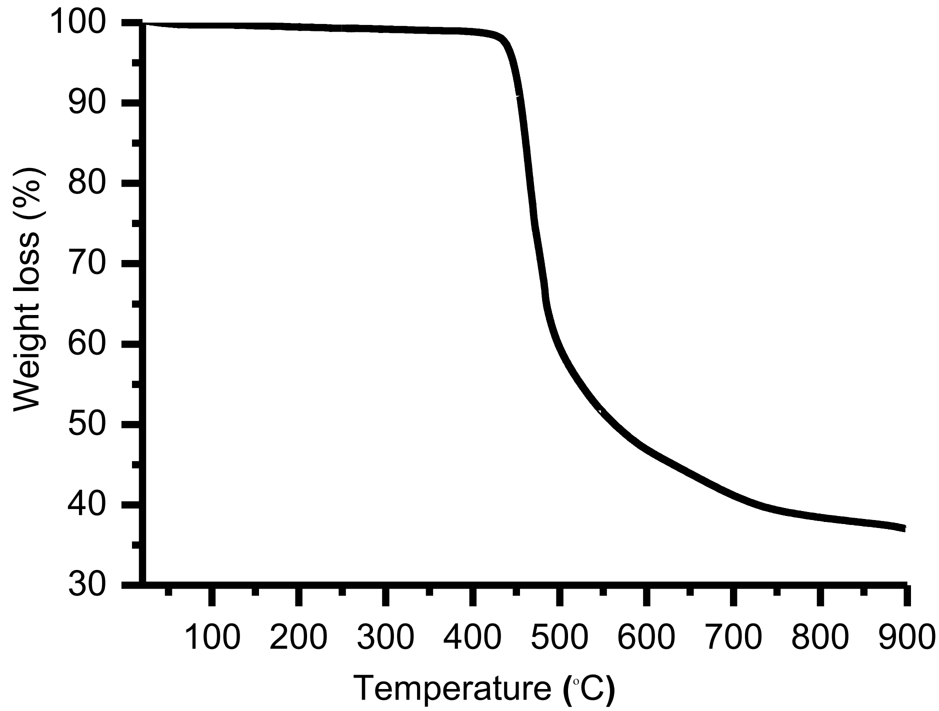


Fig. S2 Thermogravimetric (TG) curves of complex **1** at the temperature of 25−900 ºC.

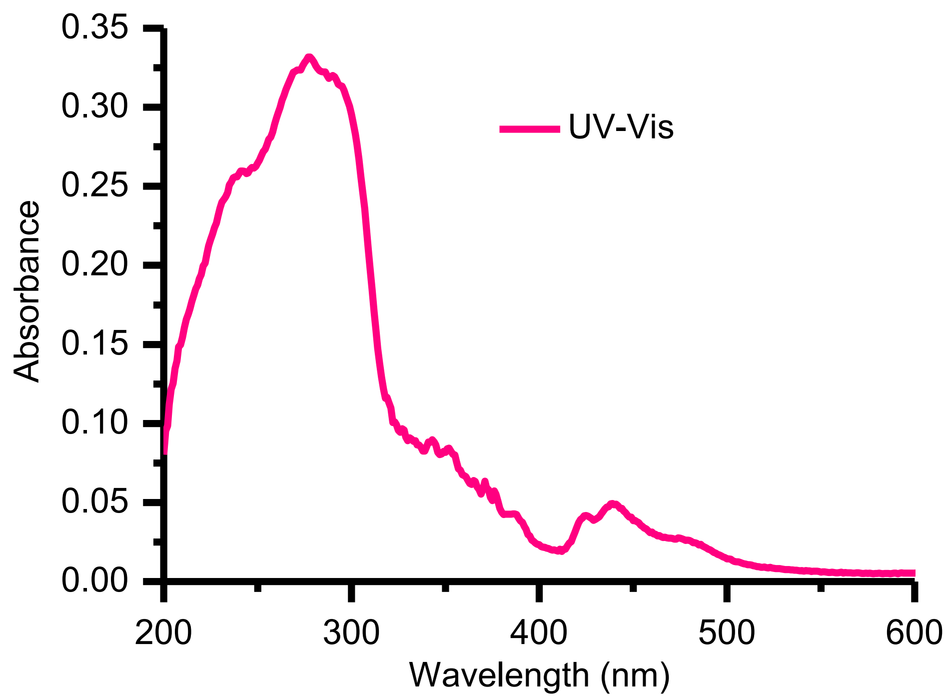


Fig. S3 The UV-Vis absorption spectrum of complex **1** in solid state at ambient temperature.

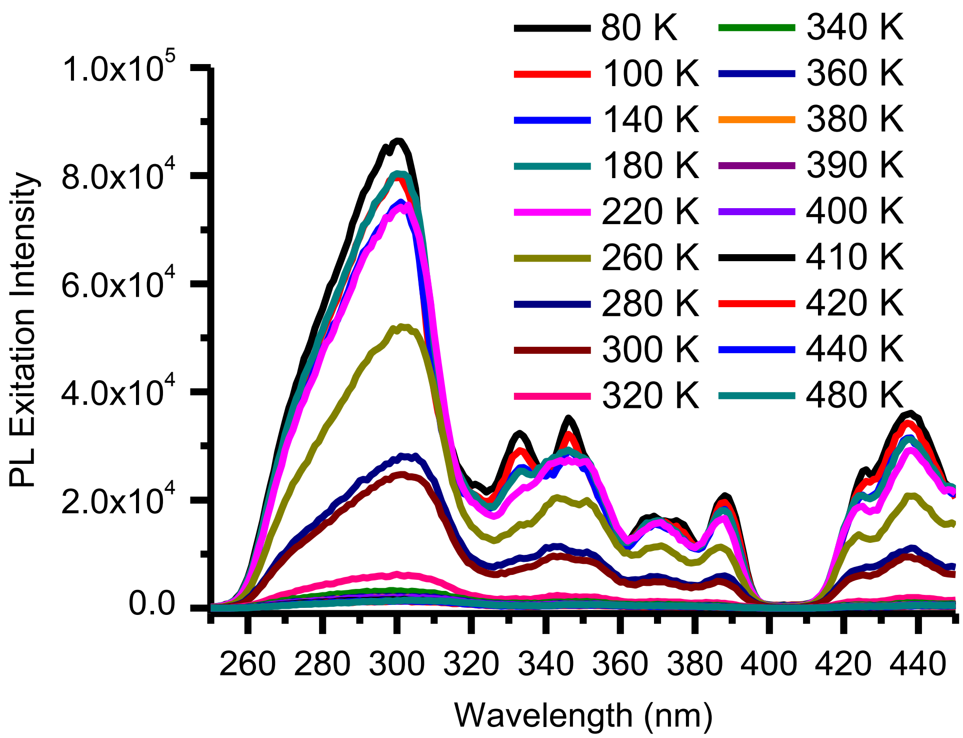


Fig. S4 The excitation spectra of complex **1** at various temperatures.

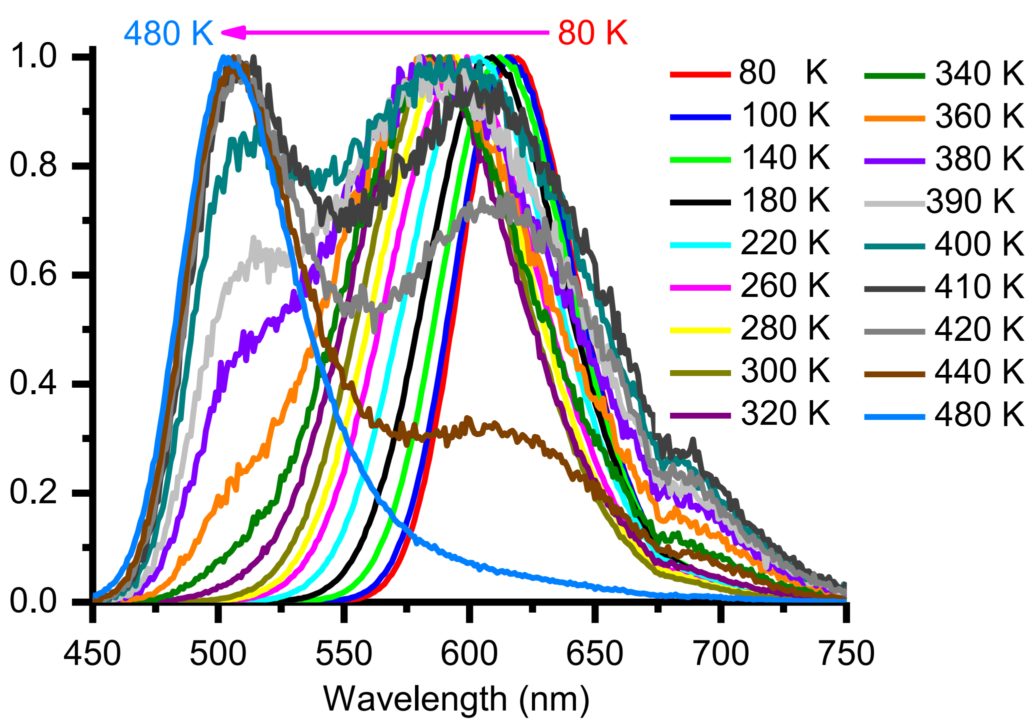


Fig. S5 The normalized emission spectral change of complex **1** upon gradually raising the temperature from 80 to 480 K.

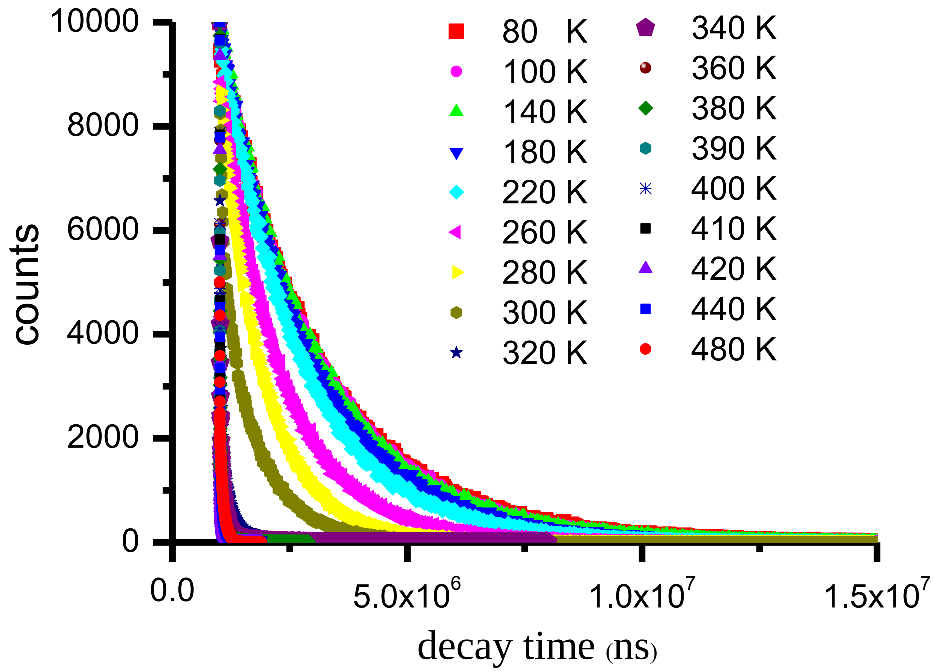
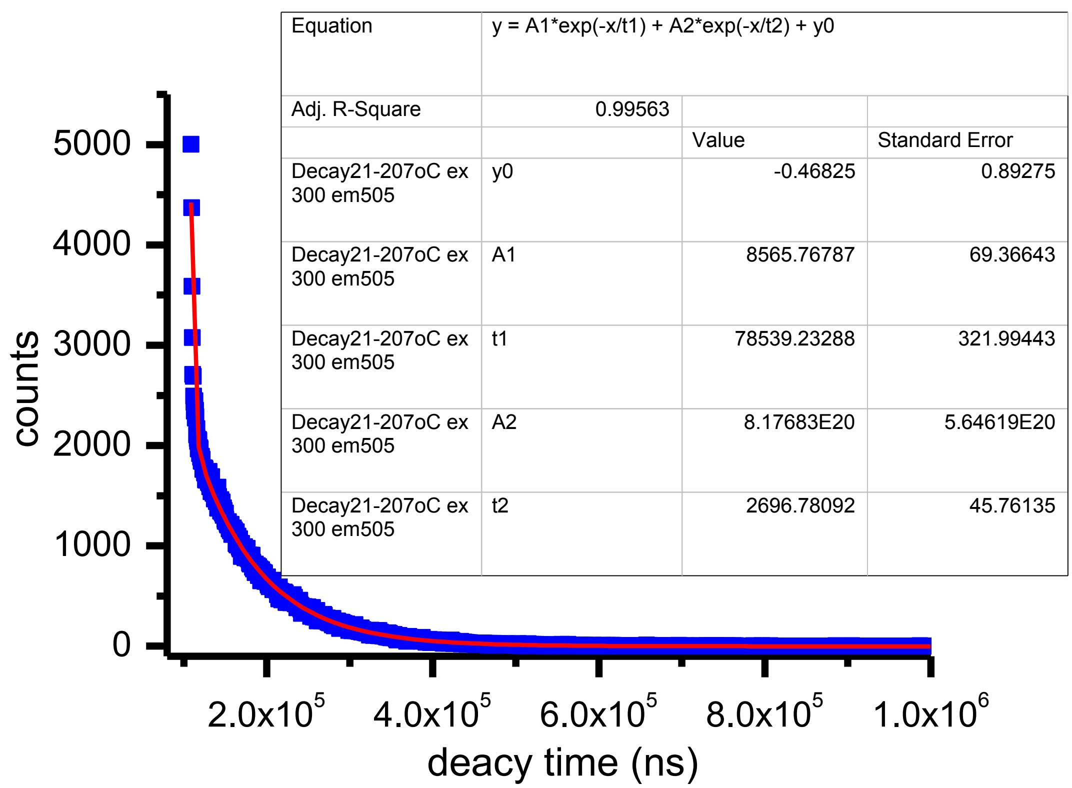


Fig. S6 The emission decay curves of complex **1** measured at various temperatures.



Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Adj. R-Square	0.99563		
		Value	Standard Error
Decay21-207oC ex 300 em505	y0	-0.46825	0.89275
Decay21-207oC ex 300 em505	A1	8565.76787	69.36643
Decay21-207oC ex 300 em505	t1	78539.23288	321.99443
Decay21-207oC ex 300 em505	A2	8.17683E20	5.64619E20
Decay21-207oC ex 300 em505	t2	2696.78092	45.76135

Fig. S7 The emission decay curve of complex **1** at 480 K, fitted by two-exponential components to give a longer emissive lifetime of 78.5 μs and shorter lifetime of 2.7 μs.

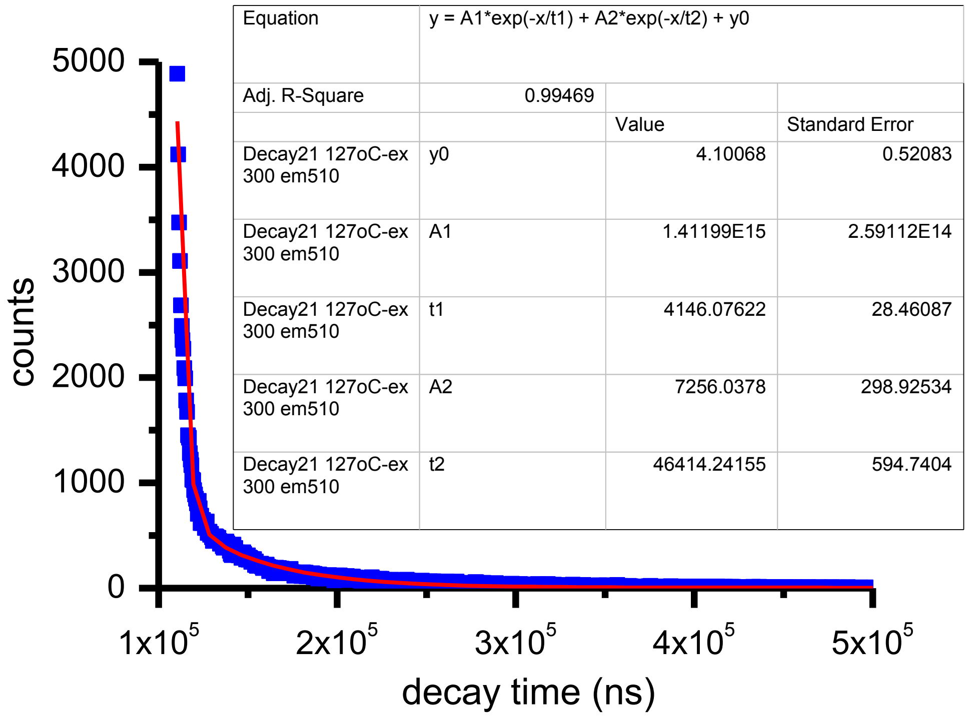


Fig. S8 The emission decay curve of complex **1** at 400 K, fitted by two-exponential components to give a longer emissive lifetime of 46.4 μs and shorter lifetime of 4.1 μs.

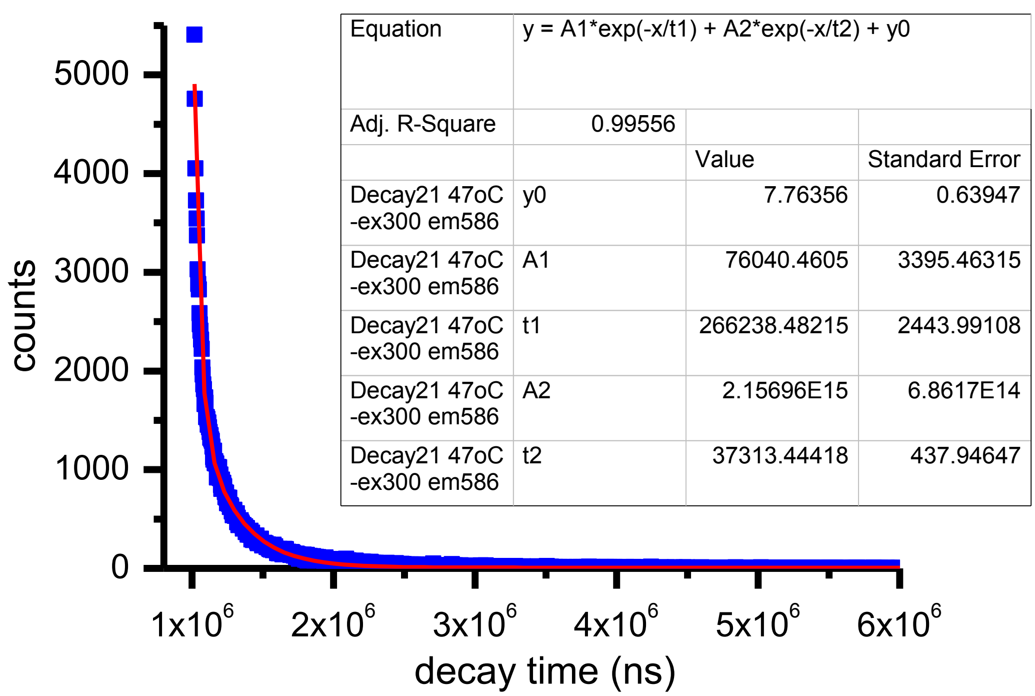


Fig. S9 The emission decay curve of complex **1** at 320 K, fitted by two-exponential components to give a longer emissive lifetime of 266 μs and shorter lifetime of 37.3 μs.

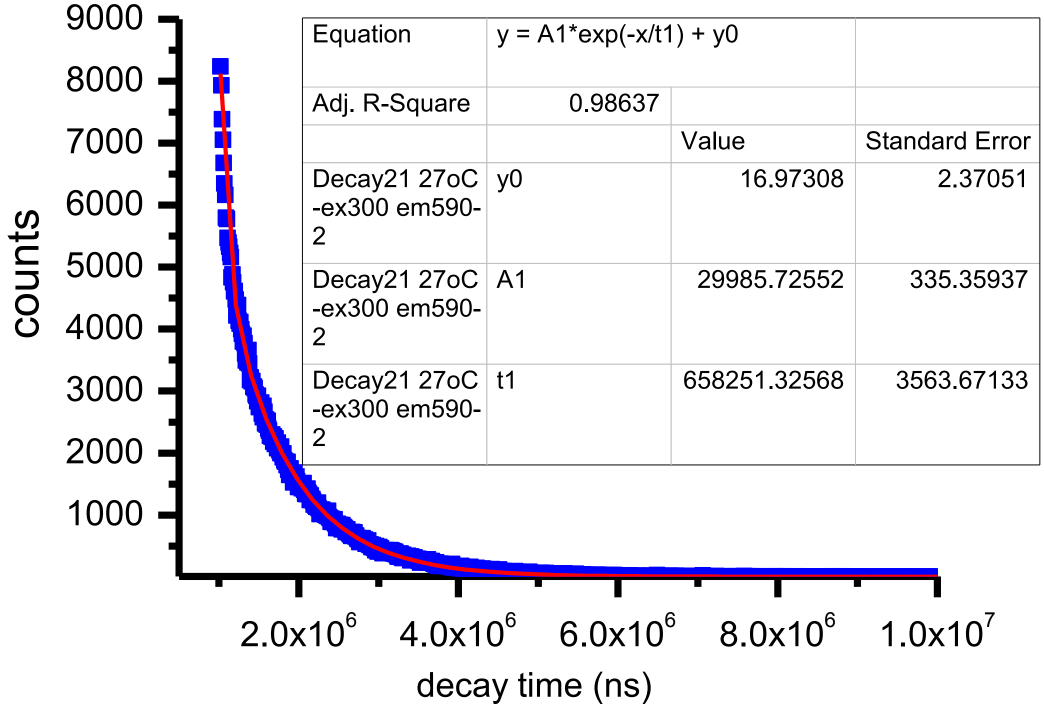


Fig. S10 The emission decay curve of complex **1** at 300 K, fitted by single exponential component to give 658 μs of emissive lifetime.

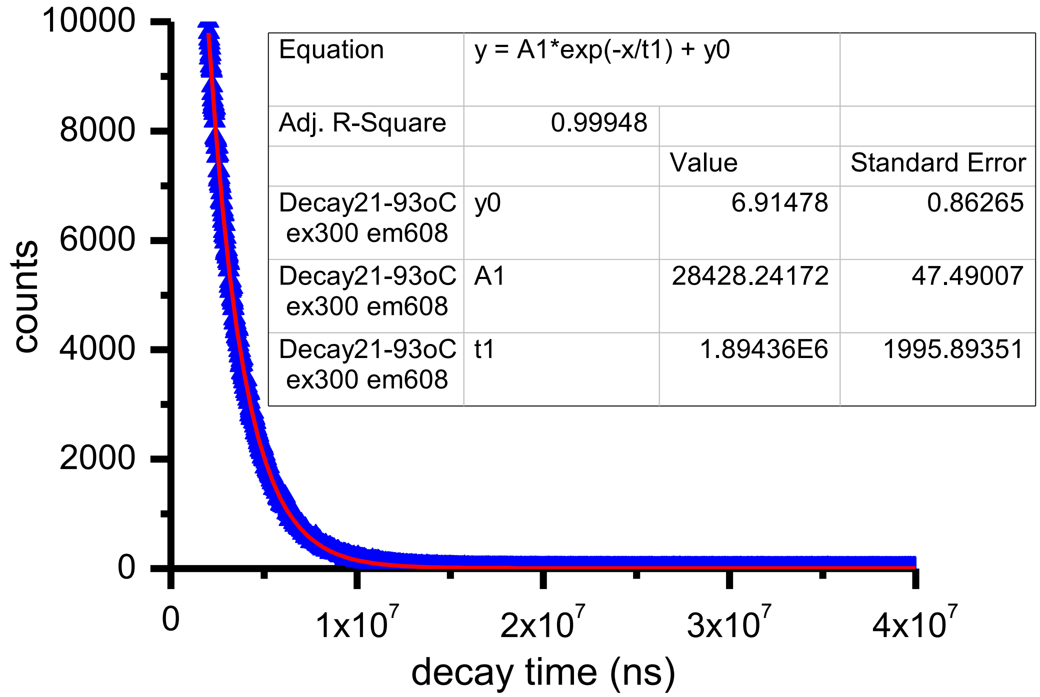


Fig. S11 The emission decay curve of complex **1** at 180 K, fitted by single exponential component to give 1894 μs of emissive lifetime.

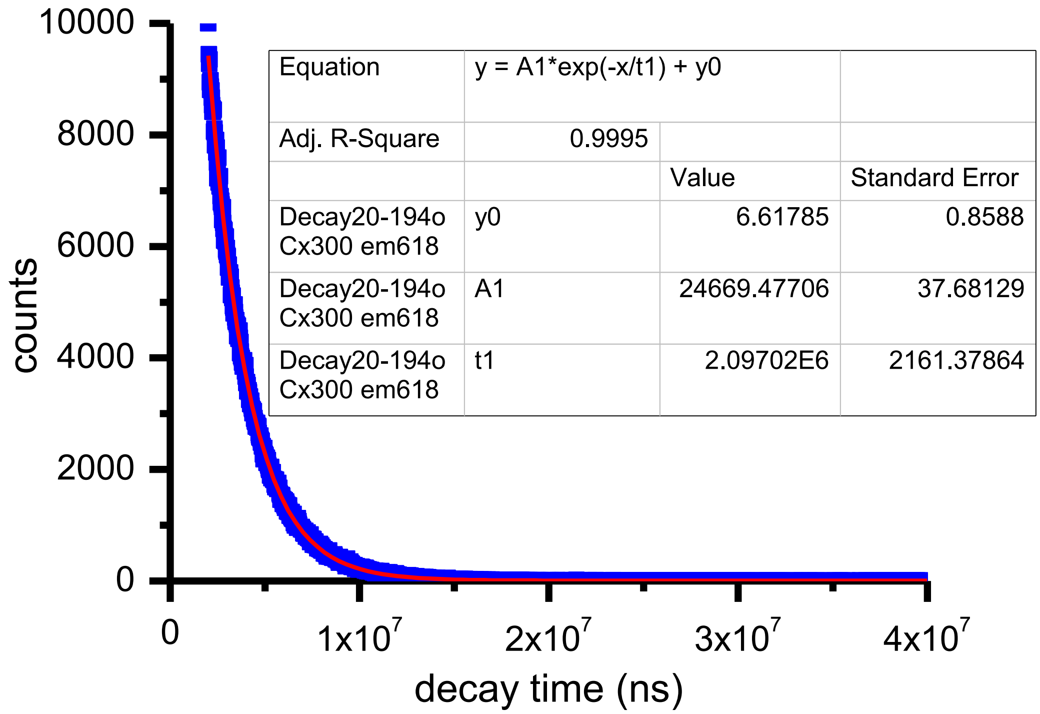


Fig. S12 The emission decay curve of complex **1** at 80 K, fitted by single exponential component to give 2097 μs of emissive lifetime.