Supporting Information for:

Steric Quenching of Mn(III) Thermal Spin Crossover: Dilution of Cooperativity in Immobilized Solutions

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Table S1 – Crystallographic details for compounds 1 – 3.

L1 = 4,6-diOMe-sal$_2$323

Compound	[Mn(L1)]ClO_4·0.5H_2O (1)	[Mn(L1)]NO_3·1.15H_2O (2)	[Mn(L1)]BF_4·0.85H_2O (3)
sample code	mor460	mor1695sqz	mor458
Empirical formula	C_{26} H_{37} N_4 $O_{10.5}$ Cl Mn	C_{26} $H_{38.30}$ N_5 $O_{10.15}$ Mn	C_{26} $H_{37.70}$ B N_4 $O_{6.85}$ F_4 Mn
Molecular formula	$[C_{26} H_{36} N_4 O_6 Mn]^+[O_4 Cl]^-$ x 0.5 (H_2 O) [a]	$[C_{26} H_{36} N_4 O_6 Mn]^+[N O_3]^-$ x 1.15 (H_2 O) [a]	$[C_{26} H_{36} N_4 O_6 Mn]^+[B F_4]^-$ x 0.85 (H_2 O) [a]
Formula weight	663.99	638.25	657.65
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (#14)	$P2_1/c$ (#15)	$P2_1/c$ (#14)
Unit cell dimensions	a = 7.4001(2) Å b = 25.9281(5) Å c = 15.8508(4) Å α = 90° β = 103.392(2)° γ = 90°	a = 7.4383(2) Å b = 25.0727(7) Å c = 15.9190(5) Å α = 90° β = 102.857(3)°. γ = 90°	a = 7.3927(2) Å b = 25.5359(5) Å c = 15.8964(4) Å α = 90° β = 103.035(3)°. γ = 90°
Volume	2958.60(12) $Å^3$	2894.43(15) $Å^3$	2923.58(12) $Å^3$
Z	4	4	4
Density (calculated)	1.491 Mg/m^3	1.465 Mg/m^3	1.494 Mg/m^3
Absorption coefficient	0.600 mm^{-1}	4.272 mm^{-1}	4.347 mm^{-1}
F(000)	1388	1342	1370
Crystal size	0.2927 x 0.1785 x 0.1047 mm^3	0.090 x 0.060 x 0.030 mm^3	0.2957 x 0.0697 x 0.0378 mm^3
Theta range for data collection	3.41 to 29.69°.	3.349 to 76.715°.	3.34 to 77.06°.
Index ranges	–10<=h<=9, –34<=k<=34, –21<=l<=21	–9<=h<=9, –29<=k<=31, –19<=l<=12	–8<=h<=9, –32<=k<=31, –19<=l<=17
Reflections collected	33572	20052	25054
Independent reflections	7424 [R(int) = 0.0229]	6026 [R(int) = 0.0437]	6113 [R(int) = 0.0404]
Completeness to theta = 26.00°	99.1 %	100.0 %	98.8 %
Absorption correction	Analytical	Gaussian	Analytical
Max. and min. transmission	0.941 and 0.884	0.951 and 0.792	0.863 and 0.415
Refinement method	Full–matrix least–squares on F^2	Full–matrix least–squares on F^2	Full–matrix least–squares on F^2
Data / restraints / parameters	7424 / 21 / 435 [b]	6026 / 0 / 383	6113 / 1 / 436 [b]
Goodness–of–fit on F^2	1.277	1.026	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0568, wR2 = 0.1216	R1 = 0.0529, wR2 = 0.1364	R1 = 0.0458, wR2 = 0.1067
R indices (all data)	R1 = 0.0623, wR2 = 0.1230	R1 = 0.0609, wR2 = 0.1426	R1 = 0.0508, wR2 = 0.1085
Largest diff. peak and hole	0.465 and –0.506 e.$Å^{-3}$	0.669 and –1.013 e.$Å^{-3}$	0.324 and –0.954 e.$Å^{-3}$
CCDC no.	2124581	2124586	2124580

Table S2 – Crystallographic details for compounds 4 & 5.

L1 = 4,6-diOMe-sal$_2$323

Compound	[Mn(L1)]CF_3SO_3 (4)	[Mn(L1)]Cl·C_2H_5OH (5)
sample code	mor474	mor1681
Empirical formula	C_{27} H_{36} N_4 O_9 F_3 S Mn	C_{28} H_{42} N_4 O_7 Cl Mn
Molecular formula	$[C_{26}$ H_{36} N_4 O_6 $Mn]^+[C$ O_3 F_3 $S]^-$	$[C_{26}$ H_{36} N_4 O_6 $Mn]^+[Cl]^-$ x C_2 H_6 O
Formula weight	704.60	637.04
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	1.54184 Å
Crystal system	Triclinic	Orthorhombic
Space group	P–1 (#2)	$P2_12_12_1$ (#19)
Unit cell dimensions	a = 7.6509(2) Å b = 13.6659(3) Å c = 14.8979(3) Å α = 81.821(2)° β = 78.568(2)° γ = 87.964(2)°	a = 7.7595(2) Å b = 17.3258(4) Å c = 21.6335(3) Å α = 90° β = 90° γ = 90°
Volume	1511.20(6) $Å^3$	2908.40(11) $Å^3$
Z	2	4
Density (calculated)	1.548 Mg/m^3	1.455 Mg/m^3
Absorption coefficient	0.584 mm^{-1}	4.979 mm^{-1}
F(000)	732	1344
Crystal size	0.3313 x 0.2396 x 0.1169 mm^3	0.230 x 0.020 x 0.020 mm^3
Theta range for data collection	3.28 to 30.63°.	3.268 to 76.893°.
Index ranges	–10<=h<=10, –19<=k<=19, –21<=l<=21	–9<=h<=9, –21<=k<=21, –27<=l<=26
Reflections collected	90343	33312
Independent reflections	9241 [R(int) = 0.0445]	6087 [R(int) = 0.0903]
Completeness to theta = 26.00°	99.2 %	100.0 %
Absorption correction	Analytical	Gaussian
Max. and min. transmission	0.947 and 0.850	1.000 and 0.562
Refinement method	Full–matrix least–squares on F^2	Full–matrix least–squares on F^2
Data / restraints / parameters	9241 / 0 / 418	6087 / 0 / 376
Goodness–of–fit on F^2	1.051	0.931
Final R indices [I>2sigma(I)]	R1 = 0.0277, wR2 = 0.0719	R1 = 0.0343, wR2 = 0.0634
R indices (all data)	R1 = 0.0318, wR2 = 0.0748	R1 = 0.0473, wR2 = 0.0677
Largest diff. peak and hole	0.510 and –0.433 e.$Å^{-3}$	0.275 and –0.258 e.$Å^{-3}$
CCDC no.	2124582	2124585

Table S3 – Crystallographic details for compounds 6 & 7.

L2 = 4,6-diOMe-sal$_2$323-C$_6$
L3 = 4,6-diOMe-sal$_2$323-C$_{12}$

Compound	$[Mn(L2)](BF_4)_{0.8}(ClO_4)_{0.2}\cdot 2CH_3OH$ (6)	$[Mn(L3)]ClO_4$ (7)
sample code	mor538	mor486
Empirical formula	$C_{40}H_{68}B_{0.79}N_4O_{8.82}F_{3.18}Cl_{0.21}Mn$	$C_{50}H_{84}N_4O_{10}Cl\ Mn$
Molecular formula	$[C_{38}H_{60}N_4O_6Mn]^+\{[BF_4]^-\}_{0.79}\{[ClO_4]^-\}_{0.21}$ x 2 (CH_4O)	$[C_{50}H_{84}N_4O_6Mn]^+[ClO_4]^-$
Formula weight	877.34	991.60
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)
Unit cell dimensions	a = 13.3746(2) Å b = 19.7053(3) Å c = 16.9698(3) Å α = 90° β = 103.383(2)° γ = 90°	a = 16.8651(4) Å b = 19.6544(3) Å c = 17.4379(4) Å α = 90° β = 118.068(3)° γ = 90°
Volume	4350.95(12) $Å^3$	5100.4(2) $Å^3$
Z	4	4
Density (calculated)	1.339 Mg/m^3	1.291 Mg/m^3
Absorption coefficient	0.386 mm^{-1}	3.068 mm^{-1}
F(000)	1870.3	2136
Crystal size	0.2140 x 0.1463 x 0.1111 mm^3	0.2379 x 0.1870 x 0.0897 mm^3
Theta range for data collection	3.34 to 24.13°.	3.73 to 77.20°.
Index ranges	–15<=h<=15, –22<=k<=22, –19<=l<=19	–17<=h<=21, –24<=k<=24, –21<=l<=18
Reflections collected	74650	59849
Independent reflections	6916 [R(int) = 0.0500]	10606 [R(int) = 0.0455]
Completeness to theta = 26.00°	99.6 %	98.0 %
Absorption correction	Analytical	Analytical
Max. and min. transmission	0.968 and 0.942	0.809 and 0.659
Refinement method	Full–matrix least–squares on F^2	Full–matrix least–squares on F^2
Data / restraints / parameters	6916 / 0 / 534	10606 / 0 / 601
Goodness–of–fit on F^2	1.074	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1339	R1 = 0.0512, wR2 = 0.1389
R indices (all data)	R1 = 0.0582, wR2 = 0.1409	R1 = 0.0595, wR2 = 0.1501
Largest diff. peak and hole	0.966 and –0.462 e.$Å^{-3}$	0.858 and –0.714 e.$Å^{-3}$
CCDC no.	2124584	2124583

Table S4 – Crystallographic details for compounds 10 – 12

L6 = 3-OMe-sal$_2$323-C$_6$
L7 = 3-OMe-sal$_2$323-C$_{12}$
L8 = 3-OMe-sal$_2$323-C$_{18}$

Compound	[Mn(L6)]PF_6 (10)	[Mn(L7)]PF_6·CH_3CN (11)	[Mn(L8)]PF_6·CH_2Cl_2 (12)
sample code	mor420	mor455	mor415
Empirical formula	C_{36} H_{56} N_4 O_4 F_6 P Mn	C_{50} H_{83} N_5 O_4 F_6 P Mn	C_{61} H_{106} N_4 O_4 F_6 P Cl_2 Mn
Molecular formula	$[C_{36}$ H_{56} N_4 O_4 $Mn]^+[F_6$ $P]^-$	$[C_{48}$ H_{80} N_4 O_4 $Mn]^+[F_6$ $P]^-$ x C_2 H_3 N	$[C_{60}$ H_{104} N_4 O_4 $Mn]^+[F_6$ $P]^-$ x C H_2 Cl_2
Formula weight	808.76	1018.12	1230.31
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	1.54184 Å	0.71073 Å	1.54184 Å
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	Pbca (#61)	P–1 (#2)	P–1 (#2)
Unit cell dimensions	a = 12.85980(8) Å b = 23.0422(1) Å c = 26.4148(1) Å α = 90° β = 90° γ = 90°	a = 10.8732(3) Å b = 11.2191(3) Å c = 23.1991(6) Å α = 95.990(2)° β = 90.914(2)° γ = 108.469(2)°	a = 10.7351(7) Å b = 11.6319(5) Å c = 27.552(1) Å α = 82.052(4)° β = 85.333(4)° γ = 71.201(5)°
Volume	7827.18(7) $Å^3$	2665.98(12) $Å^3$	3223.1(3) $Å^3$
Z	8	2	2
Density (calculated)	1.373 Mg/m^3	1.268 Mg/m^3	1.268 Mg/m^3
Absorption coefficient	3.746 mm^{-1}	0.345 mm^{-1}	3.190 mm^{-1}
F(000)	3408	1088	1320
Crystal size	0.2159 x 0.0564 x 0.0462 mm^3	0.3190 x 0.2242 x 0.1602 mm^3	0.2784 x 0.1151 x 0.0267 mm^3
Theta range for data collection	3.35 to 76.80°.	3.38 to 26.44°.	4.04 to 63.99°.
Index ranges	–12<=h<=15, –27<=k<=28, –32<=l<=33	–13<=h<=13, –14<=k<=14, –29<=l<=29	–12<=h<=12, –13<=k<=13, –32<=l<=32
Reflections collected	77882	44120	49482
Independent reflections	8191 [R(int) = 0.0379]	10905 [R(int) = 0.0319]	10329 [R(int) = 0.0480]
Completeness to theta = 26.00°	99.3 %	99.2 %	96.4 %
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.856 and 0.604	0.961 and 0.929	0.941 and 0.675
Refinement method	Full–matrix least–squares on F^2	Full–matrix least–squares on F^2	Full–matrix least–squares on F^2
Data / restraints / parameters	8191 / 0 / 473	10905 / 0 / 673	10329 / 0 / 716
Goodness–of–fit on F^2	1.057	1.078	1.092
Final R indices [I>2sigma(I)]	R1 = 0.0297, wR2 = 0.0769	R1 = 0.0438, wR2 = 0.1179	R1 = 0.0555, wR2 = 0.1627
R indices (all data)	R1 = 0.0369, wR2 = 0.0793	R1 = 0.0556, wR2 = 0.1225	R1 = 0.0629, wR2 = 0.1681
Largest diff. peak and hole	0.667 and –0.447 e.$Å^{-3}$	0.892 and –0.443 e.$Å^{-3}$	1.544 and –1.220 e.$Å^{-3}$
CCDC no.	2124578	2124579	2124577

*Table S5 – Raman vibration modes of complexes (**10**) – (**12**) collected at room temperature.*

Formula	(**10**)	(**11**)	(**12**)
Raman Shifts (cm^{-1})	237	237	237
	-	302	303
	350	351	349
	367	368	369
	-	582	569
	624	626	625
	741	742	741
	862	869	866
	1295	1308	1300
	1342	1342	1340
	1442	1445	1444
	1471	1474	1474
	1596	1597	1597
	1624	1617	1617

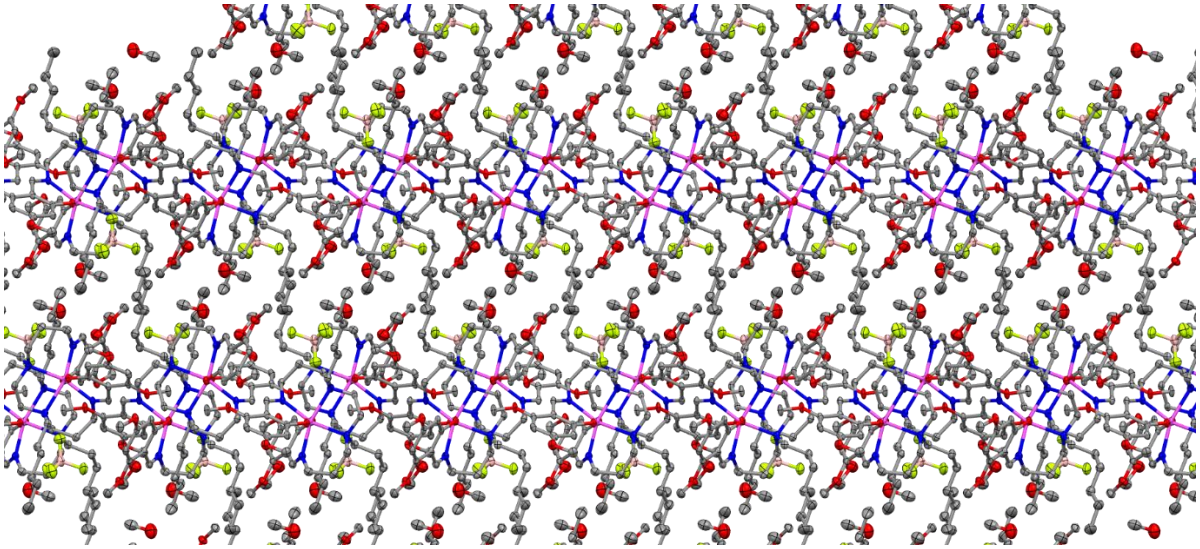

Figure S1 – C_6-Alkylated complex 6 viewed along b-axis

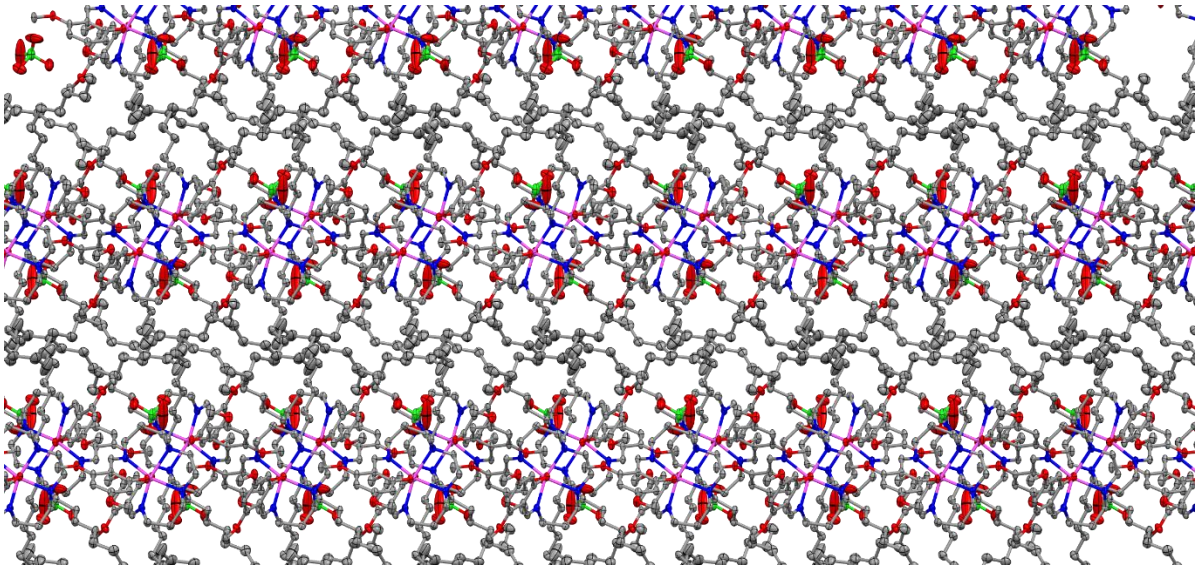

Figure S2 – C_{12}-Alkylated complex 7 viewed along the b-axis

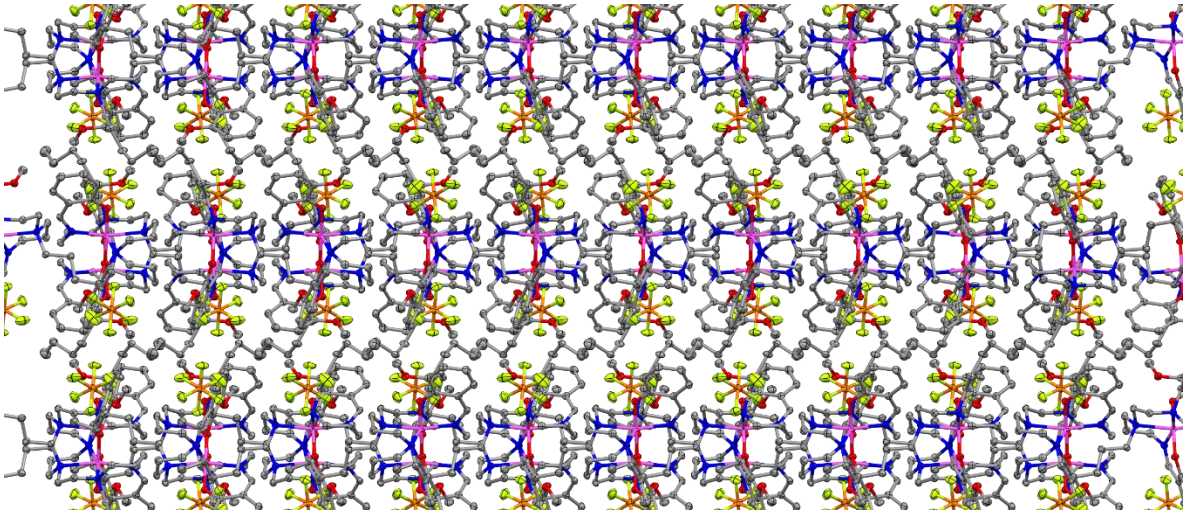

Figure S3 – C_6-Alkylated complex 10 viewed along the c-axis

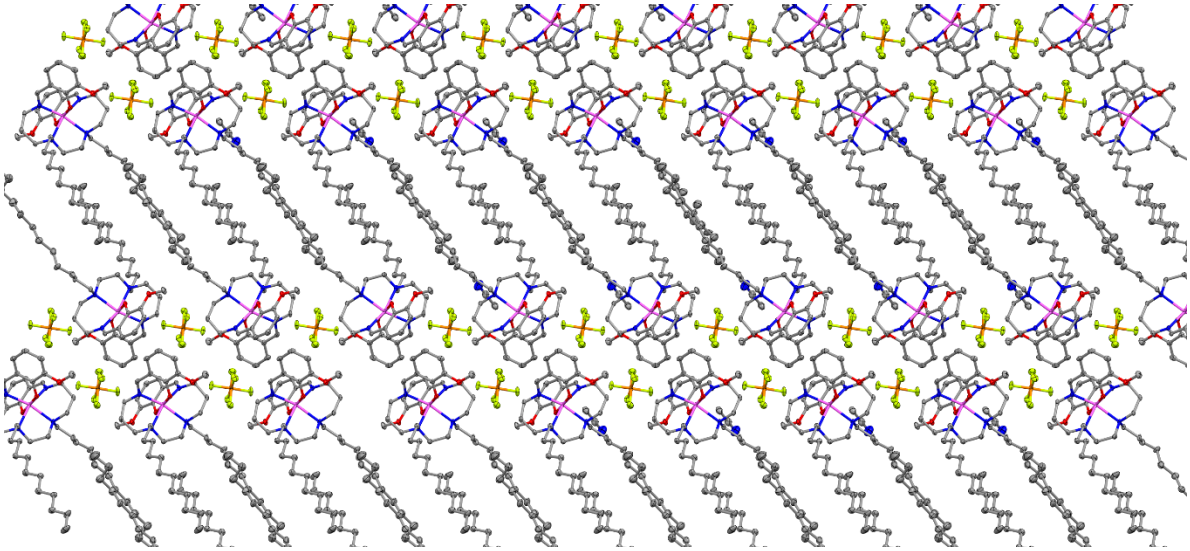

Figure S4 – C_{12}-Alkylated complex 11 viewed along the a-axis