Tetra- and dinuclear manganese complexes of xanthene-bridged O,N,O-Schiff bases with 3-hydroxypropyl or 2-hydroxybenzyl groups: ligand substitution at a triply bridging site

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Table S1. Crystallographic data for [**3**]$(ClO_4)_2$, [**4**]BF_4, and **5**

	[**3**]$(ClO_4)_2 \cdot 2^iPr_2O \cdot 5H_2O$	[**4**]$BF_4 \cdot 2CH_2Cl_2 \cdot H_2O$	**5**$\cdot 2.6C_7H_8 \cdot 4.7H_2O$
Empirical formula	$C_{82}H_{106}Cl_2Mn_2N_4O_{25}$	$C_{76}H_{77}BCl_4F_4Mn_4N_4O_{16}$	$C_{104.20}H_{94.20}Mn_2N_4O_{14.70}$
Formula weight	1728.53	1750.78	1747.51
Temperature/K	188	123	133
Wavelength/Å	0.7107	0.7107	0.7107
Crystal system	triclinic	monoclinic	tetragonal
Space group	$P\bar{1}$	$P2_1$	$P4/n$
a/Å	11.0476(15)	13.2444(13)	27.3689(9)
b/Å	13.524(2)	17.0667(17)	27.3689(9)
c/Å	15.220(3)	16.6189(17)	12.0350(5)
α/°	103.322(6)	90	90
β/°	92.830(5)	91.476(3)	90
γ/°	105.832(4)	90	90
V/Å^3	2113.5(6)	3755.3(7)	9014.9(7)
Z	1	2	4
D_{calcd}/Mg·m^{-3}	1.358	1.548	1.288
μ(Mo Kα)/mm^{-1}	0.440	0.880	0.348
F(000)	910	1796	3660
Crystal size/mm^3	0.30 × 0.20 × 0.10	0.24 × 0.21 × 0.06	0.21 × 0.17 × 0.14
Reflections collected	20828	36416	97041
Independent reflections	9616 (R_{int} = 0.0797)	16171 (R_{int} = 0.0469)	10238 (R_{int} = 0.0487)
Completeness to θ	99.1% (θ = 27.48°)	98.3% (θ = 27.48°)	99.1% (θ = 27.46°)
Max. and min. transmission	0.957 and 0.331	1.0000 and 0.8290	1.0000 and 0.9230
No. of data/restraints/parameters	9616/6/566	16171/1/1043	10238/15/590
Goodness of fit on F^2	1.052	1.031	1.107
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0899	R1 = 0.0707	R1 = 0.0685
R indices (all data)	wR2 = 0.2755	wR2 = 0.1913	wR2 = 0.2002
Absolute structure parameter		0.480(11)	
Largest diff. peak and hole (e·Å^{-3})	0.74 and –0.58	0.963 and –0.730	1.128 and –0.426

Table S2. Selected bond distances/Å and angles/° for [**3**]$(ClO_4)_2$

Mn(1)–O(1)	2.236(3)	Mn(1)–O(4)	2.305(3)
Mn(1)–O(2)	1.857(3)	Mn(1)–O(4)*	1.927(3)
Mn(1)–N(1)	2.024(4)	Mn(1)–N(2)*	2.043(4)
Mn(1)–Mn(1)*	3.3269(13)		
O(1)–Mn(1)–O(2)	97.34(14)	O(1)–Mn(1)–O(4)	165.82(12)
O(1)–Mn(1)–O(4)*	90.35(13)	O(1)–Mn(1)–N(1)	82.48(15)
O(1)–Mn(1)–N(2)*	92.50(15)	O(2)–Mn(1)–O(4)	95.83(14)
O(2)–Mn(1)–O(4)*	171.98(15)	O(2)–Mn(1)–N(1)	89.78(15)
O(2)–Mn(1)–N(2)*	90.28(15)	O(4)–Mn(1)–O(4)*	76.74(13)
O(4)–Mn(1)–N(1)	92.36(15)	O(4)–Mn(1)–N(2)*	92.66(15)
O(4)*–Mn(1)–N(1)	93.50(15)	O(4)*–Mn(1)–N(2)*	87.09(15)
N(1)–Mn(1)–N(2)*	174.94(17)	Mn(1)–O(4)–Mn(1)*	103.26(13)
Mn(1)–O(4)–C(30)	123.8(3)	Mn(1)*–O(4)–C(30)	120.9(3)

Table S3. Selected bond distances/Å and angles/° for **5**

Mn(1)–O(1)	1.8991(19)	Mn(1)–O(3)*	1.8941(19)
Mn(1)–O(2)	1.8862(18)	Mn(1)–O(4)*	1.8813(19)
Mn(1)–N(1)	1.999(2)	Mn(1)–N(2)*	1.991(2)
Mn(1)–Mn(1)*	8.1499(8)		
O(1)–Mn(1)–O(2)	178.78(8)	O(1)–Mn(1)–O(3)*	88.07(8)
O(1)–Mn(1)–O(4)*	88.88(8)	O(1)–Mn(1)–N(1)	89.69(8)
O(1)–Mn(1)–N(2)*	91.60(8)	O(2)–Mn(1)–O(3)*	90.92(8)
O(2)–Mn(1)–O(4)*	92.13(8)	O(2)–Mn(1)–N(1)	90.97(8)
O(2)–Mn(1)–N(2)*	87.71(8)	O(3)*–Mn(1)–O(4)*	176.91(8)
O(3)*–Mn(1)–N(1)	89.29(9)	O(3)*–Mn(1)–N(2)*	89.41(9)
O(4)*–Mn(1)–N(1)	90.24(9)	O(4)*–Mn(1)–N(2)*	91.14(9)
N(1)–Mn(1)–N(2)*	178.13(9)		

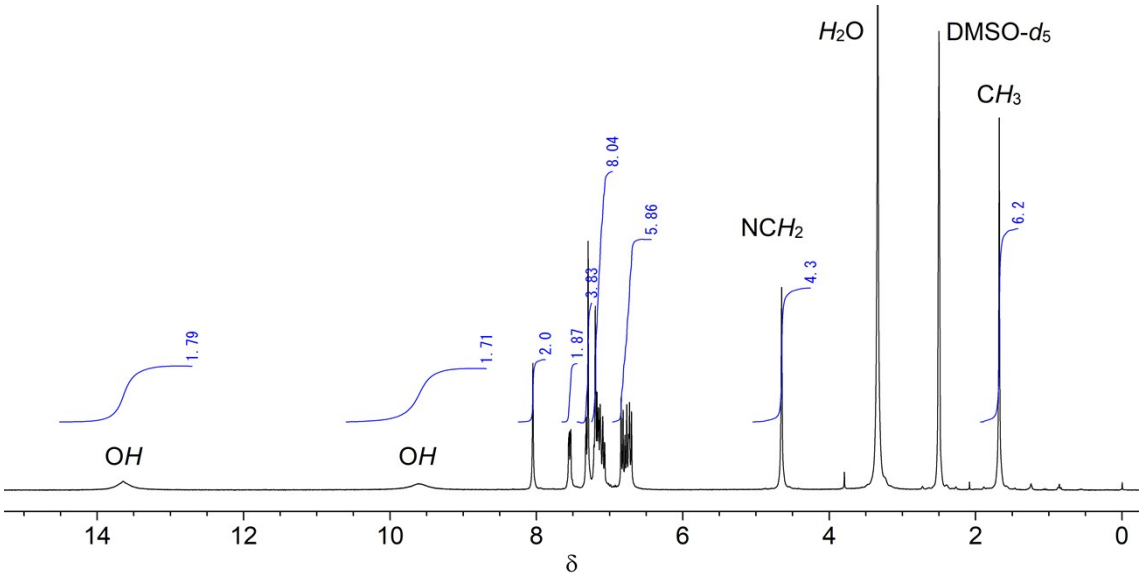

Fig. S1. ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of H_4L^2.

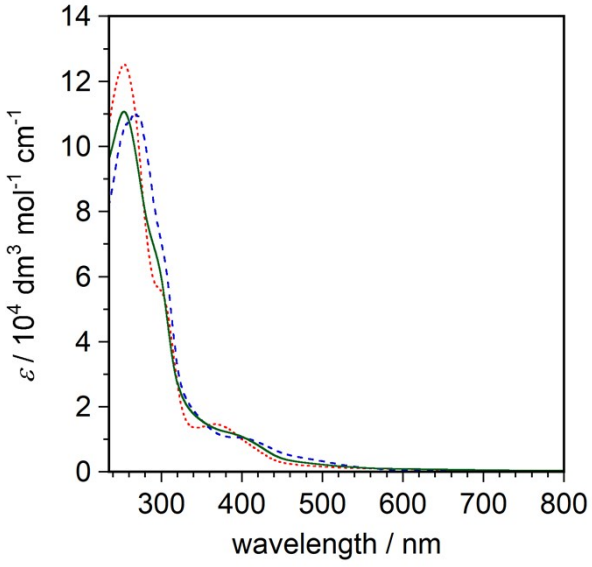

Fig. S2. Absorption spectra of tetramanganese complexes **1** (·····),[1] **2** (- - -),[1] and [**4**]BF_4 (—) in dichloromethane.

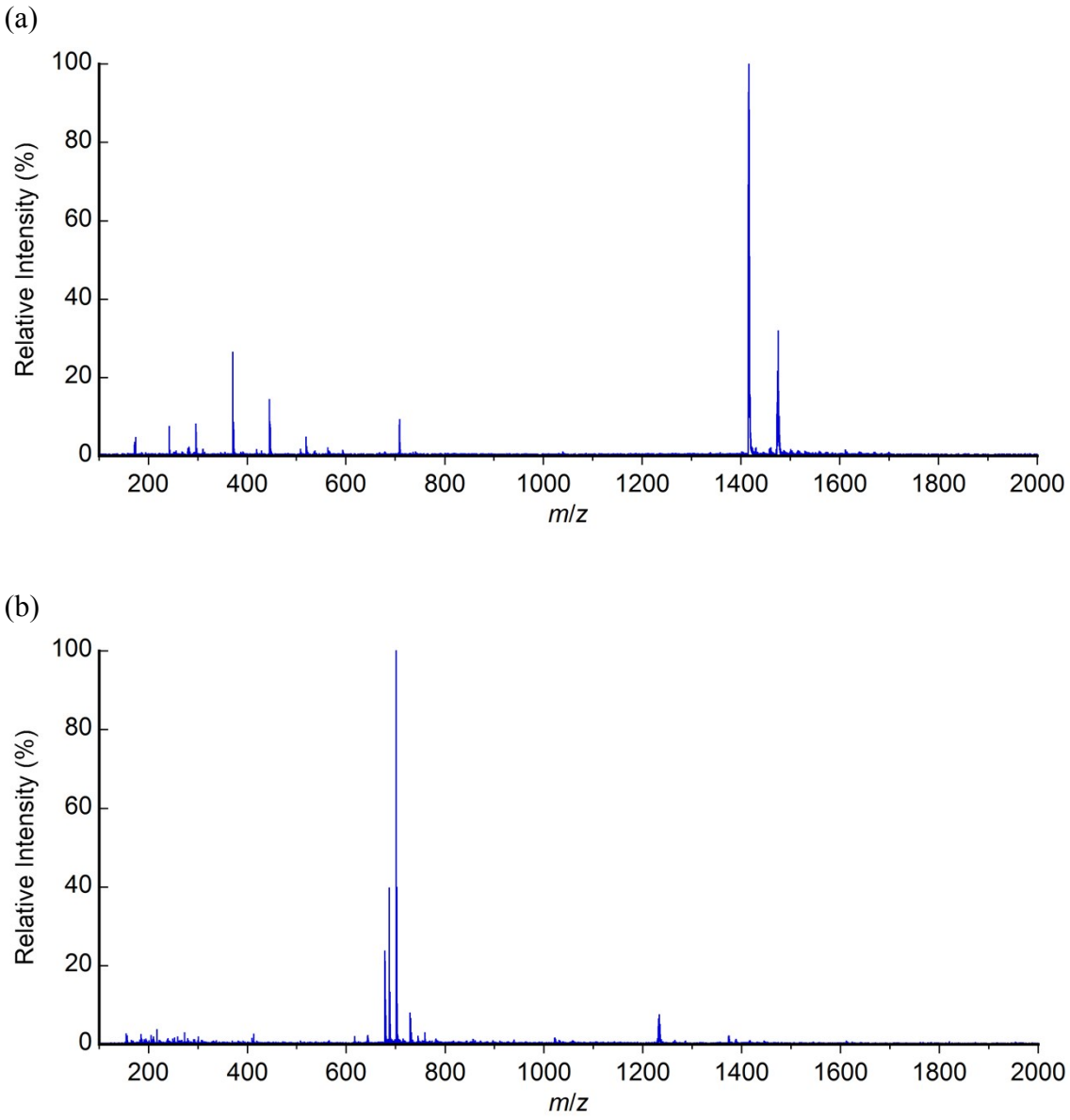

Fig. S3. ESI mass spectra of [**4**](BF_4) in (a) dichloromethane and (b) methanol.

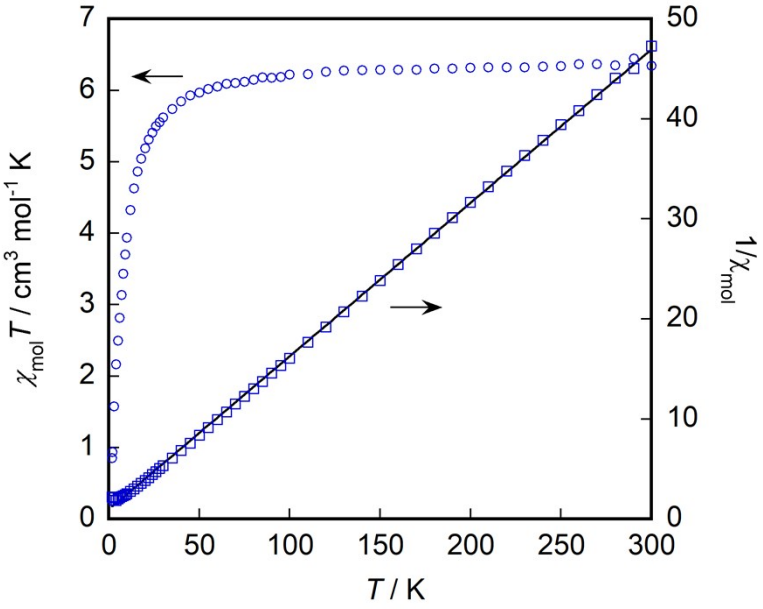

Fig. S4. Temperature dependence of χT and $1/\chi$ for [**3**]$(ClO_4)_2$. Solid lines represent the least-squares fits of the data to the model described in the text.

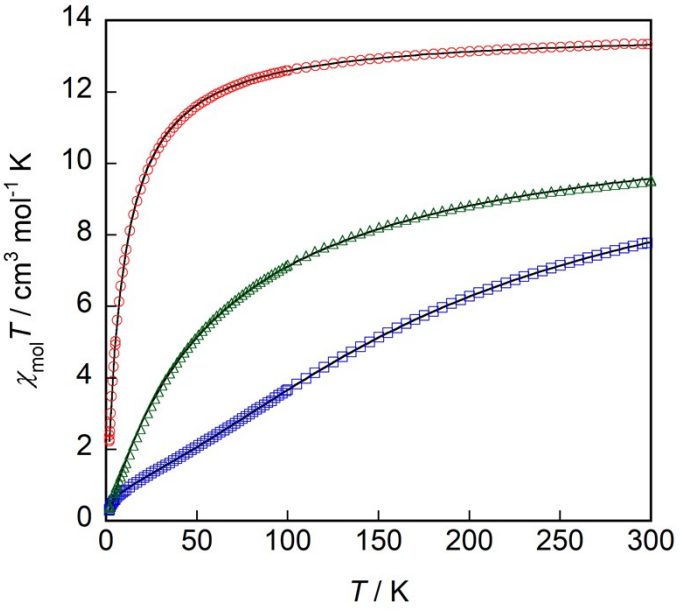

Fig. S5. Temperature dependence of χT for **1** (○),[1] **2** (□),[1] and [**4**](BF_4) (△). Solid lines represent the least-squares fits of the data to the model described in the text.

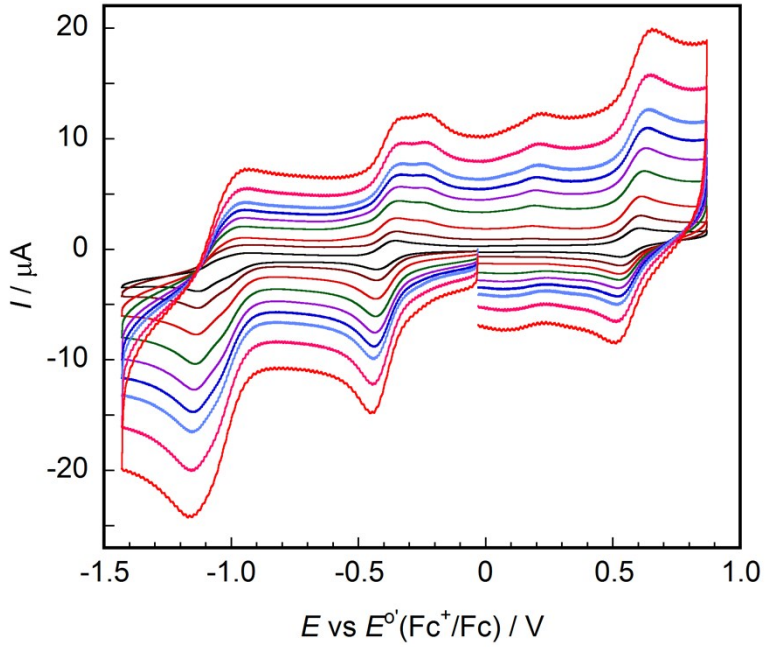

Fig. S6. Cyclic voltammograms of [**4**]PF_6 (2.3×10^{-4} M) in CH_2Cl_2 containing 0.1 M Bu_4NPF_6: scan rate, 20 (black), 50 (dark brown), 100 (red brown), 200 (green), 300 (purple), 400 (blue), 500 (light blue), 700 (pink), 1000 (red) mV s^{-1}; working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, Ag/Ag^+. Potentials are versus ferrocenium/ferrocene (Fc^+/Fc).

Reference

1) M. Hirotsu, Y. Shimizu, N. Kuwamura, R. Tanaka, I. Kinoshita, R. Takada, Y. Teki and H. Hashimoto, *Inorg. Chem.*, 2012, **51**, 766–768.