Supporting Information

Mn_4-Hinged Bithiacalix[4]arenes Accommodating Fullerenes

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Experimental Section

Materials and Measurements: Phenyl-thiacalix[4]arene (H_4PTC4A) was synthesized by literature method[1] and other reagents were purchased from commercial sources and used as received. Mn and S analyses were determined by a HITACHI S-4800 Scanning Electron Microscope. Fluorescence spectra were obtained on a Hitachi F-4700 fluorescence/phosphorescence spectrophotometer. UV measurements were collected using a Hitachi U-4100 spectrophotometer; BaSO4 powder was used as the reference (100% reflectance). X-ray diffraction (XRD) measurements were performed on a Bruker D8 Focus diffractometer.

Synthesis of 1-3:

Colorless single crystals of **1** and a few orange sheets of **1**' were obtained from reaction of the mixture of phenylthiacalix[4]arene (0.1g, 0.125 mmol), $Mn(CH_3COO)_2{\cdot}4H_2O$ (0.1 g, 0.4 mmol), $CHCl_3$ (5 ml), CH_3OH (5ml) and several drops of water in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 20 °C at about 4 °C/h. The crystals were isolated by filtration and then washed with 1:1 methanol-chloroform. Yield: ca. 65 % for **1** with respect to H_4PTC4A. The EDS analysis of **1** reveals that the molar ratio of Mn to S molar is 2.50:4.94, comparable to the expected value (4:8).

2a and **2b** formed by slowly diffusing fullerenes (1.8/2.1 mg for C_{60}/C_{70}, 2.5×10^{-3} mmol in 2

ml toluene, respectively) to **1** (20mg, 1×10^{-2} mmol in 10 ml toluene). Dark-red octahedron crystals suitable for X-ray diffraction obtained after about three days, respectively. Due to the small amount original components used, calculations of the yields of **2a** and **2b** are meaningless.

The mixture **1** (20 mg, 1×10^{-2} mmol) with C_{60} (3.6 mg, 5×10^{-3} mmol) in 30ml toluene afford 7.7 mg red crystal blocks of **3**. The crystals were isolated by filtration and then washed small amount of cooling toluene. Yield: ca. 95 % with respect to C_{60}.

[1] P. Lhoták, T. Šmejkal, I. Stibor, J. Havlíček, M. Tkadlecovč, H. Petříčková, *Tetrahedron Lett.* 2003, **44**, 8093.

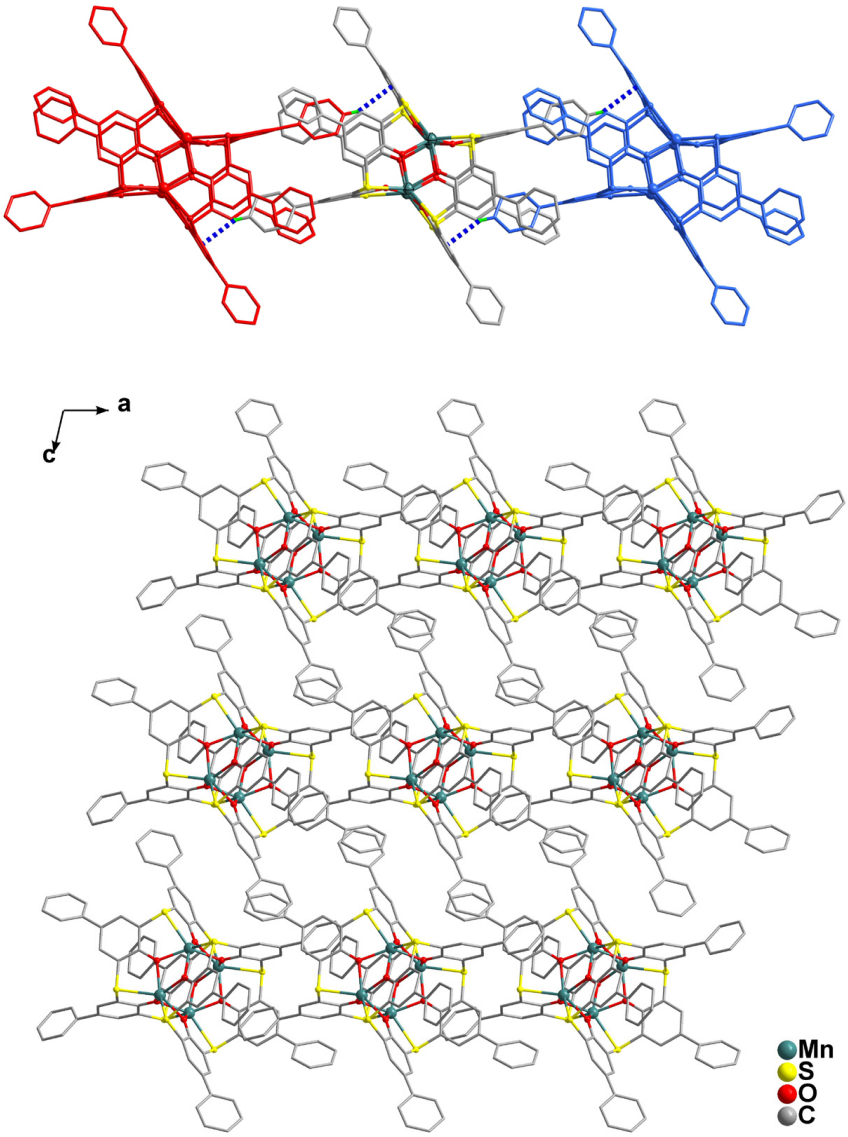


Figure S1. 'Hand-shake' dumbbell units linked by C–H···π interactions (upper) and the extended structure (bottom) of **1**.

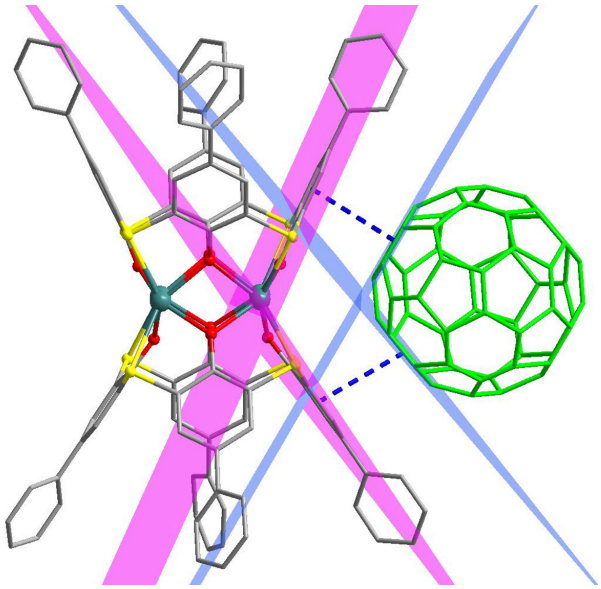


Fig. S2 Contact mode between $Mn_4(PTC4A)_2$ and C_{60}. Blue dotted lines: π···π interactions.

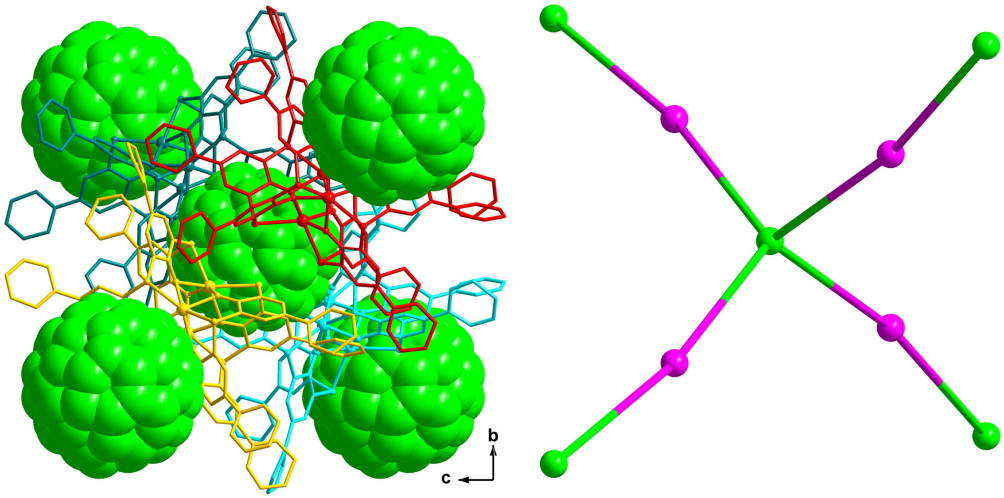


Fig. S3 Assembly mode between $Mn_4(PTC4A)_2$ units (purple balls) and fullerenes (green balls, C_{60} or C_{70})

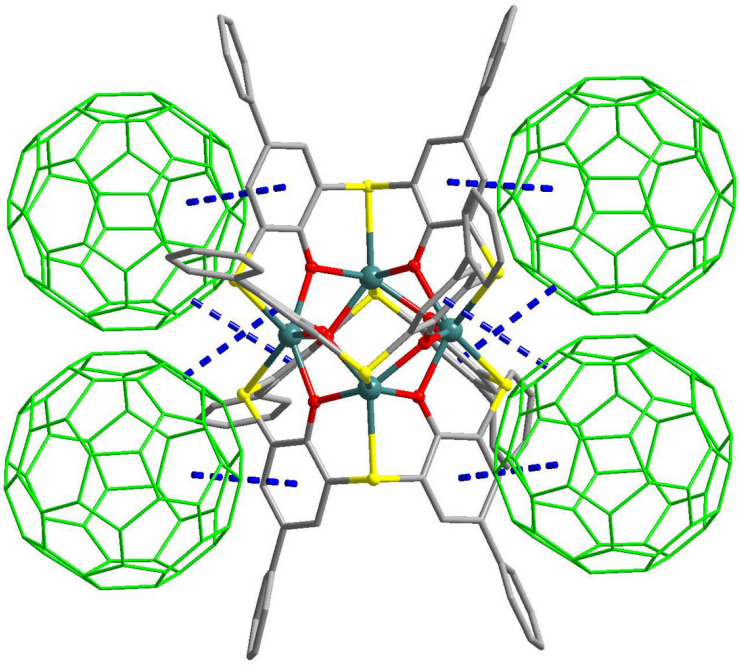


Fig. S4 $Mn_4(PTC4A)_2$ capturing four C_{60} molecules by all four curved surfaces by π···π interactions in **3**.

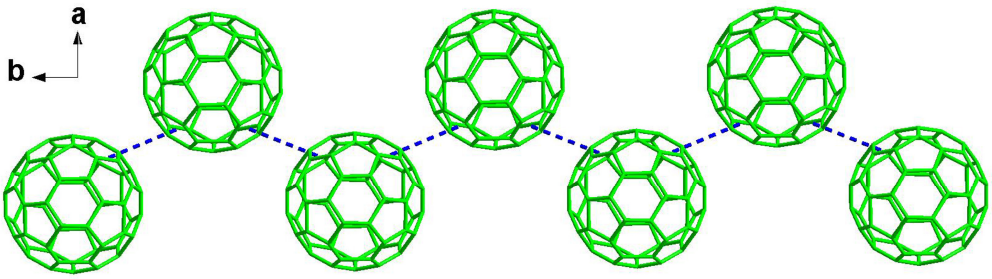


Fig. S5 π···π interactions between C_{60} molecules in **3**.

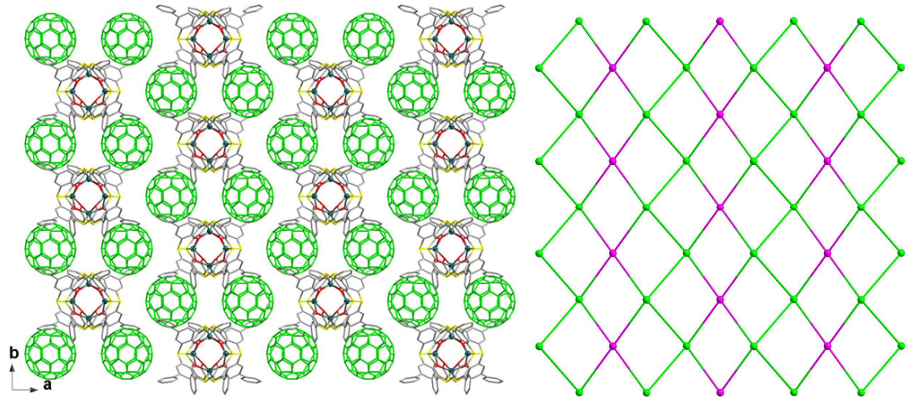


Fig. S6 Layer structure (left) and the topology diagram (right) in **3**.

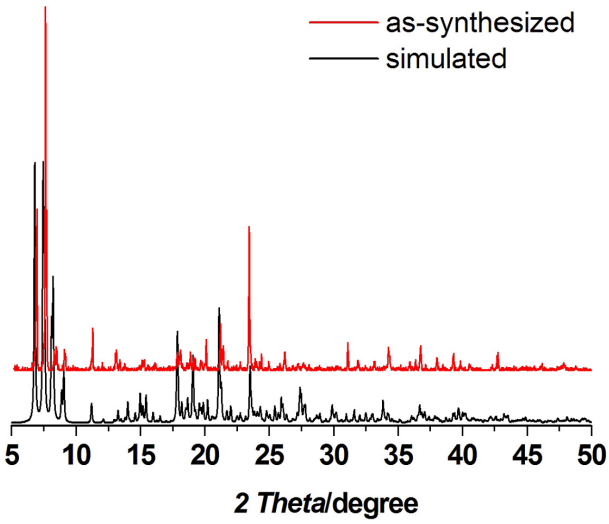


Fig. S7 Stimulated and experimental X-ray diffraction (XRD) patterns of **1**. The slight differences may be due to lose of $CHCl_3$ in the crystalline samples at room temperature.

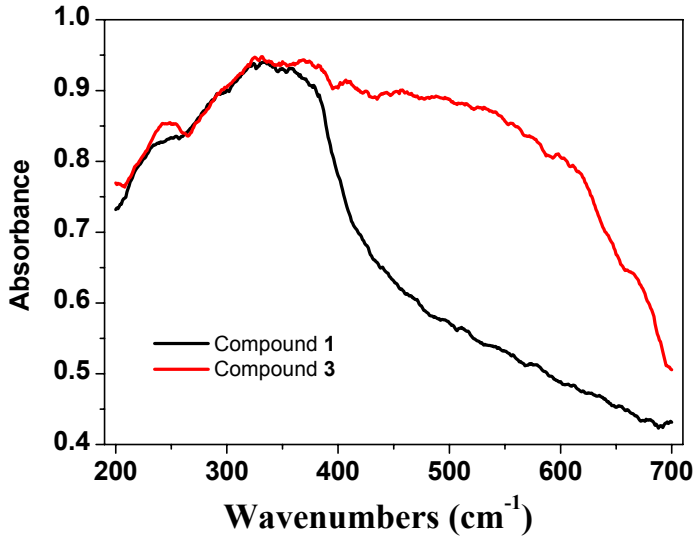


Fig. S8 UV-absorption spectra of compounds **1** and **3.**

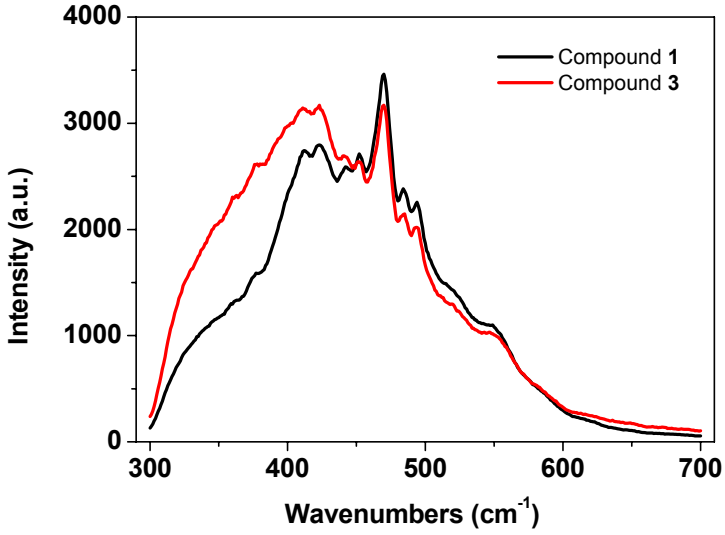


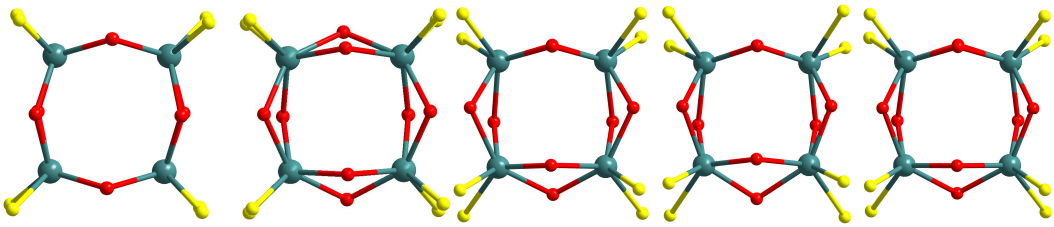
Fig. S9 Emission spectra (λ_{ex} = 260 nm) of **1** and **3** in the solid state at room temperature showing similar emission bands.

Table S1. Crystal data and structure refinement for compounds **1-3**

	1	**1'**	**2a**	**2b**	**3**
formula	$C_{98}H_{58}Cl_6Mn_4O_8S_8$	$C_{96}H_{56}Mn_4O_8S_8$	$C_{252}H_{112}Mn_8O_{16}S_{16}$	$C_{262}H_{112}Mn_8O_{16}S_{16}$	$C_{216}H_{56}Mn_4O_8S_8$
formula wt.	2052.38	1813.65	4347.90	4468.00	3254.85
Cryst. syst	Triclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
space group	$P\bar{1}$	$P2_1/c$	$Fdd2$	$Fdd2$	$C2/c$
a (Å)	13.2061(6)	15.1007(8)	56.211(3)	57.682(2)	33.470(2)
b (Å)	13.6364(6)	21.877(1)	29.843(2)	30.018(1)	14.4254(9)
c (Å)	14.9448(7)	23.903(1)	30.793(2)	30.768(1)	37.212(2)
α (°)	117.052(1)	90	90	90	90
β (°)	90.389(1)	99.005(1)	90	90	90.300(1)
γ (°)	113.035(1)	90	90	90	90
V (Å ^{3})	2148.9(2)	7799.6(7)	51655 (5)	53275(4)	17966(2)
Z	1	4	8	8	4
T(K)	173(2)	173(2)	187(2)	187(2)	185(2)
D_c/g cm^{-3}	1.586	1.545	1.118	1.114	1.203
μ/mm^{-1}	1.016	0.910	0.560	0.545	0.426
F(000)	1040	3696	17664	18144	6576
Tot. Data	10999	39674	90912	94251	70547
Uniq. Data	7512	13720	21881	23419	15913
R_{int}	0.0175	0.0704	0.1546	0.1514	0.0569
GOF	1.146	1.015	0.948	0.956	0.991
$R1^a$ [$I>2\sigma(I)$]	0.0614	0.0517	0.0869	0.0877	0.0612
$wR2^b$[$I>2\sigma(I)$]	0.1615	0.1137	0.2144	0.2176	0.1718

$^a R1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; $^b wR2 = \{\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$

Table S2. Selected bond distances (Å) and angles (º) for Mn ions in Compounds **1**-**3**



1 **1'** **2a** **2b** **3**

1		**1'**	
Mn(1)–O(1)	2.097(3)	Mn(1)-O(1)	2.103(3)
Mn(1)–O(2)^{A}	2.154(3)	Mn(1)-O(8)	2.124(3)
Mn(1)–O(3)^{A}	2.120(3)	Mn(1)-O(4)	2.142(3)
Mn(1)–O(4)	2.128(3)	Mn(1)-O(5)	2.181(3)
Mn(1)–S(1)	2.7209(13)	Mn(1)-S(8)	2.6245(13)
Mn(1)–S(3)^{A}	2.6983(12)	Mn(1)-S(4)	2.6527(13)
Mn(2)–O(1)	2.129(3)	Mn(2)-O(1)	2.103(3)
Mn(2)–O(2)	2.130(3)	Mn(2)-O(6)	2.124(3)
Mn(2)–O(3)^{A}	2.110(3)	Mn(2)-O(2)	2.130(3)
Mn(2)–O(4)^{A}	2.158(4)	Mn(2)-O(5)	2.172(3)
Mn(2)–S(2)	2.6940(13)	Mn(2)-S(5)	2.6735(13)
Mn(2)–S(4)^{A}	2.7319(13)	Mn(2)-S(1)	2.7188(13)
		Mn(3)-O(6)	2.119(3)
Mn(1)–O(1) –Mn(2)	103.61(13)	Mn(3)-O(3)	2.119(3)
Mn(1)^{A}–O(3) –Mn(2)^{A}	103.47(13)	Mn(3)-O(7)	2.163(3)
Mn(1)^{A}–O(2) –Mn(2)	103.27(13)	Mn(3)-O(2)	2.170(3)
Mn(1)–O(4) –Mn(2)^{A}	103.18(13)	Mn(3)-S(2)	2.6858(13)
		Mn(3)-S(6)	2.7021(13)
		Mn(4)-O(8)	2.098(3)
		Mn(4)-O(3)	2.123(3)
		Mn(4)-O(7)	2.163(3)
		Mn(4)-O(4)	2.179(3)
		Mn(4)-S(3)	2.7343(13)
		Mn(4)-S(7)	2.7593(13)

		Mn(1)-O(1)-Mn(2)	103.88(12)
		Mn(2)-O(2)-Mn(3)	100.87(12)
		Mn(3)-O(3)-Mn(4)	102.68(12)
		Mn(4)-O(4)-Mn(1)	98.98(12)
		Mn(2)-O(5)-Mn(1)	99.06(11)
		Mn(3)-O(6)-Mn(2)	102.78(12)
		Mn(4)-O(7)-Mn(3)	99.95(11)
		Mn(4)-O(8)-Mn(1)	102.21(12)
	2a		**2b**
Mn(1)–O(1)	2.18(2)		2.163(6)
Mn(1)–O(4)	2.09(2)		2.117(6)
Mn(1)–O(5)	2.073(18)		2.101(5)
Mn(1)–O(8)	2.176(18)		2.198(5)
Mn(1)–S(1)	2.685(8)		2.697(2)
Mn(1)–S(5)	2.646(9)		2.651(2)
Mn(2)–O(1)	2.15(2)		2.158(6)
Mn(2)–O(2)	2.142(19)		2.127(6)
Mn(2)–O(5)	2.094(18)		2.111(6)
Mn(2)–O(6)	2.175(17)		2.187(6)
Mn(2)–S(2)	2.679(9)		2.688(3)
Mn(2)–S(6)	2.689(9)		2.690(3)
Mn(3)–O(2)	2.117(19)		2.118(6)
Mn(3)–O(3)	2.18(2)		2.175(6)
Mn(3)–O(6)	2.188(19)		2.177(6)
Mn(3)–O(7)	2.08(2)		2.086(6)
Mn(3)–S(3)	2.715(9)		2.721(3)
Mn(3)–S(7)	2.677(8)		2.678(3)
Mn(4)–O(3)	2.19(2)		2.155(6)
Mn(4)–O(4)	2.131(18)		2.135(6)
Mn(4)–O(7)	2.09(2)		2.099(5)
Mn(4)–O(8)	2.179(19)		2.154(6)
Mn(4)–S(4)	2.699(9)		2.694(3)

Mn(4)–S(8)	2.659(9)	2.683(3)
Mn(1)–O(1) –Mn(2)	99.5(9)	100.1(2)
Mn(1)–O(4) –Mn(4)	102.4(8)	101.7(2)
Mn(1)–O(5) –Mn(2)	104.9(8)	103.7(2)
Mn(1)–O(8) –Mn(4)	98.3(8)	98.5(2)
Mn(3)–O(2) –Mn(2)	101.0(8)	102.0(3)
Mn(3)–O(3) –Mn(4)	98.3(9)	99.8(2)
Mn(3)–O(6) –Mn(2)	97.7(8)	98.3(2)
Mn(3)–O(7) –Mn(4)	105.3(9)	104.6(2)

3

Mn(1)–O(1)	2.112(2)	Mn(2)–O(1)	2.116(2)
Mn(1)–O(4)	2.161(2)	Mn(2)–O(2)	2.160(2)
Mn(1)–S(1)	2.7348(9)	Mn(2)–O(3)^{A}	2.120(2)
Mn(3)–O(2)	2.159(2)	Mn(2)–O(4)^{A}	2.160(2)
Mn(3)–O(3)^{A}	2.123(2)	Mn(2)–S(2)	2.6671(10)
Mn(3)–S(3)	2.7436(10)	Mn(2)–S(4)^{A}	2.6777(10)
Mn(1)–O(1) –Mn(2)	103.68(9)	Mn(1)–O(4) –Mn(2)^{A}	100.62(9)
Mn(2)–O(2) –Mn(3)	100.63(9)	Mn(2)^{A}–O(3) –Mn(3)	103.11(10)

A: -x,-y,-z for **1** and -x,y,1/2-z for **3**