Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Material (ESI) for "*Syntheses, structures, chiroptical and magnetic properties of chiral clusters built from Schiff bases: a novel [$Mn^{II}Mn^{III}{}_6Na^{I}{}_2$] core* "

Syntheses and methods.

H_2L ligand: A solution 0.072 M of the H_2L ligand was previously prepared following the procedure: 0.5 g (3.64 mmols) of the corresponding *R* or *S* enantiomer of 2-phenylglycinol and 0.55 g (3.64 mmols) of 2-hydroxy-3-methoxybenzaldehyde in 20 mL of methanol. The yellow mixture was refluxed for 1 h and diluted to 50 mL with methanol. This solution was employed directly in the synthesis of the derived complexes.

Complexes 1*R* and 1*S*: $MnBr_2·4H_2O$ (0.104 g, 0.365 mmols) and NaN_3 (0.024 g, 0.365 mmols) dissolved in 20 mL of acetonitrile were added to 5 mL of the previous prepared ligand solution of H_2L (0.365 mmols). The mixture was stirred at room temperature for three hours, filtered and layered with diethylether. Dark brown crystals were collected after a week. Analogous reaction starting from $MnCl_2·4H_2O$ lead to complexes **2**. Anal. Calcd for $C_{217} H_{233} Br_{16} Mn_{16} N_{21} Na_4 O_{49}$ (**1*R***): C, 42.25; H, 3.81; N, 4.77%. Found: C, 42.0; H, 3.6; N, 4.4%, (corresponding to the partial loss of around 2 ACN). Anal. Calcd for $C_{220} H_{234} Br_{16} Mn_{16} N_{24} Na_4 O_{53}$ (**1*S***): C, 41.86; H, 3.74; N, 5.33%. Found: C, 41.6; H, 3.7; N, 4.7%,(corresponding to the partial loss of around 4 ACN).

Complexes 2*R* and 2*S*: $MnCl_2·4H_2O$ (0.072 g., 0.365 mmols) and NaOH (0.015 g, 0.365 mmols) were dissolved in 20 mL of acetonitrile and stirred for 5 minutes. After that, 5 mL of the H_2L ligand solution (0.365 mmols) were added. The resulting mixture was stirred at room temperature for 3 h and filtered. The resulting solution was layered with diethylether and dark brown crystals were obtained after few days. Anal. Calcd for $C_{105} H_{111}Cl_6 Mn_7 N_6 Na_2 O_{23}$ (**2*R***): C, 50.24; H, 4.46; N, 5.02%. Found: C, 50.5; H, 4.1; N, 4.8% (corresponding to the partial loss of around 2 ACN and one methanol). Anal. Calcd for $C_{97.5} H_{100} Cl_6 Mn_7 N_6 Na_2 O_{23.5}$ (**2*S***): C, 49.30; H, 4.24; N, 3.542%. Found: C, 49.4; H, 3.7; N, 4.3%.

Complex 3*R*: was obtained following the same procedure, starting from $MnBr_2·4H_2O$ instead $MnCl_2·4H_2O$. Anal. Calcd for $C_{108} H_{112} Br_6 Mn_7 N_{10} Na_2 O_{21}$ (**3*R***): C, 46.03; H, 3.94; N, 4.13%. Found: C, 45.8; H, 3.8; N, 4.3% (corresponding to the loss of the diethylether and partial loss of around 2 ACN).

The reaction that allow to the pentanuclear complexes **1*R***/**1*S*** was also performed starting from manganese chloride but this reaction produces in all cases compounds **2*R***/**2*S*** instead the pentanuclear clusters. In contrast, the syntheses of the enneanuclear complexes **2*R***/**2*S***/**3*R*** is not sensitive to the starting halide salt.

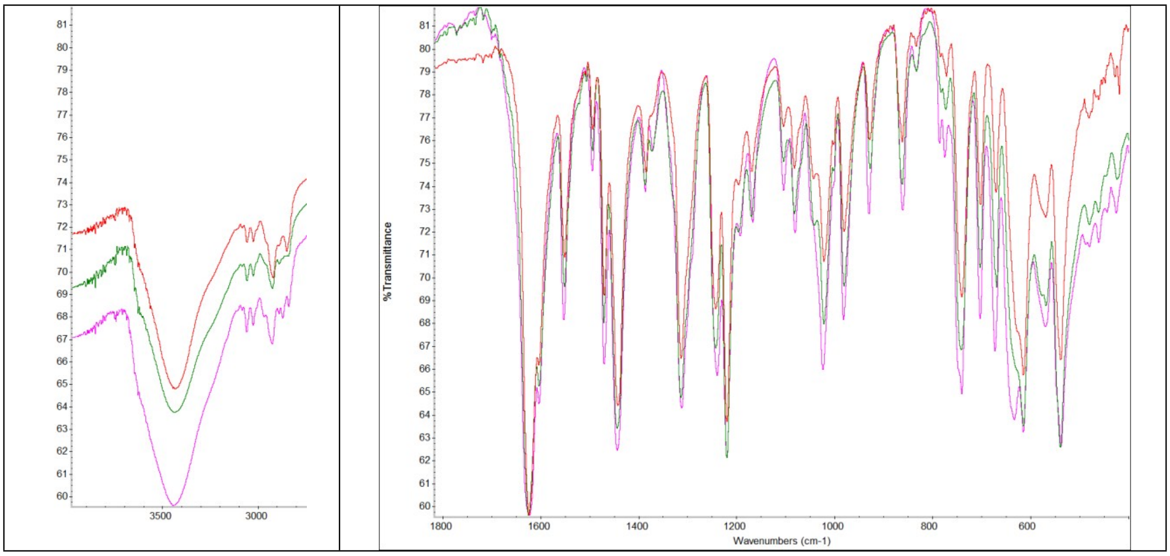

Fig S1. IR spectra for one of the enantiomers of **1** (red), **2** (violet) and **3** (green). As can be expected from the similar subunits and analogous coordination of the Schiff base, the spectra do not show differences between the penta and nonanuclear complexes. The only relevant difference corresponds to the peak at 635 cm^{-1} for the chloro complex **2** that shifts to 614 cm^{-1} for the bromo complexes **1** and **3**.

Instrumental measurements

IR spectra (4000-400 cm-1) were recorded using a Bruker IFS-125 FT-IR spectrometer with samples prepared as KBr pellets. Variable-temperature magnetic studies were performed using a MPMS-5 Quantum Design magnetometer operating at 0.03 T in the 300-2.0 K range. Diamagnetic corrections were applied to the observed paramagnetic susceptibility using Pascal's constants. Analysis of the magnetic data were performed with PHI program. ECD and UV-Vis spectra were recorded using a Jasco J-715 spectrometer at room temperature in spectroscopy grade acetonitrile in three quartz cells with path-length of 2 cm (850-450 nm), 1 cm (450-315 nm), and 0.1 cm (315-200 nm). The solid-state ECD spectra were obtained by placing a KBr pellet in a rotating holder as close as possible to the photomultiplier tube of a Jasco J-715 spectrometer. The X-ray intensity data were measured on a D8-Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The final cell constants were based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The structures were solved using the Bruker SHELXTL Software Package, and refined using SHELXL.

Table S1. Crystal data and structure refinement for coordination compounds **1*R*** and **1*S***.

	1*R*	**1*S***
Formula	$C_{217}H_{233}Br_{16}Mn_{16}N_{21}Na_4O_{49}$	$C_{220}H_{234}Br_{16}Mn_{16}N_{24}Na_4O_{53}$
FW	6168.79	6311.86
System	Triclinic	Monoclinic
Space group	P1	P21
a/Å	16.545(2)	20.2507(7)
b/Å	19.911(2)	16.3807(6)
c/Å	20.663(2)	20.7092(8)
α/deg.	114.549(4)	90
β/deg.	91.914(5)	115.848(1)
γ/deg.	90.337(4)	90
V/ Å^3	6187(1)	6182.4(4)
Z	1	1
T, K	100(2)	100(2)
λ(MoKα), Å	0.71073	0.71073
ρcalc, g·cm-3	1.656	1.695
μ(MoK$_\alpha$), mm^{-1}	3.450	3.456
R	0.0536	0.0361
ωR^2	0.1344	0.0762

Table S2. Crystal data and structure refinement for coordination compounds **2*R***, **2*S*** and **3*R***.

	2*R*	**2*S***	**3*R***
Formula	$C_{105}H_{111}Cl_6Mn_7N_6Na_2O_{23}$	$C_{97.5}H_{100}Cl_6Mn_7N_6Na_2O_{23.5}$	$C_{108}H_{112}Br_6Mn_7N_{10}Na_2O_{21}$
FW	2510.28	2375.09	2796.09
System	Trigonal	Trigonal	Triclinic
Space group	R3	R3	P1
a/Å	19.6260(7)	19.686(1)	14.2067(6)
b/Å	19.6260(7)	19.686(1)	14.5629(7)
c/Å	28.7679(9)	28.677(2)	16.5401(8)
α/deg.	90	90	91.435(2)
β/deg.	90	90	112.245(2)
γ/deg.	120	120	110.988(2)
V/ Å^3	9596.3(7)	9624(2)	2905.6(2)
Z	3	3	1
T, K	100(2)	100(2)	100(2)
λ(MoKα), Å	0.71073	0.71073	0.71073
ρcalc, g·cm-3	1.303	1.229	1.598
μ(MoK$_\alpha$), mm^{-1}	0.864	0.857	2.876
R	0.0572	0.0441	0.0304
ωR^2	0.1654	0.1137	0.0730

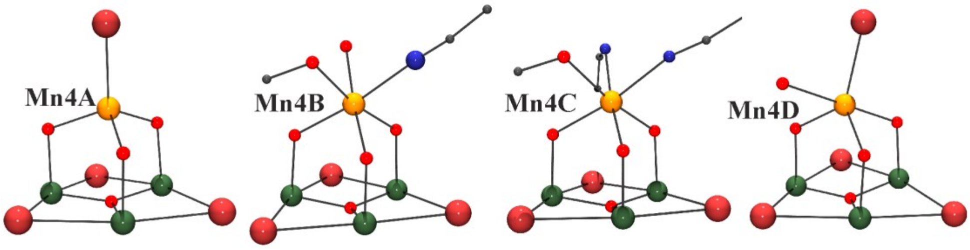

Fig S2. Detail of the coordination of the divalent atom Mn4 in the four non-equivalent units of **1*R***. The structure of **1*S*** contains two non-equivalent units similar to B and D.

Table S3. Selected bond distances (Å) and angles (°) for the core of compounds **1*R*** and **1*S***.

	(1*R*)-A	**(1*R*)-B**	**(1*R*)-C**	**(1*R*)-D**	**(1*S*)-A**	**(1*S*)-B**
Coordination number for Mn4	4	6	6	5	5	6
Mn1-O10	1.928(8)	1.893(9)	1.931(9)	1.891(8)	1.890(4)	1.905(5)
Mn2-O10	1.880(8)	1.884(9)	1.894(9)	1.898(9)	1.895(4)	1.887(5)
Mn3-O10	1.915(9)	1.873(9)	1.844(9)	1.877(8)	1.905(5)	1.894(5)
Mn1-O1	1.905(10)	1.875(9)	1.899(8)	1.881(8)	1.900(5)	1.892(4)
Mn2-O4	1.895(10)	1.878(10)	1.899(8)	1.898(9)	1.901(5)	1.897(5)
Mn3-O7	1.893(10)	1.881(9)	1.879(9)	1.886(9)	1.904(5)	1.880(4)
Mn4-O1	2.079(9)	2.145(9)	2.160(9)	2.183(8)	2.166(5)	2.157(5)
Mn4-O4	2.082(9)	2.133(11)	2.153(8)	2.059(9)	2.086(5)	2.151(5)
Mn4-O7	2.017(11)	2.136(10)	2.100(10)	2.076(9)	2.071(5)	2.148(5)
Mn1-O10-Mn2	121.5(5)	119.1(5)	117.3(5)	116.2(4)	2.128(3)	118.0(2)
Mn1-O10-Mn3	119.5(4)	118.0(5)	120.4(4)	118.7(5)	2.162(3)	118.7(2)
Mn2-O10-Mn3	118.6(4)	120.5(5)	120.3(5)	123.1(4)	2.230(2)	120.6(2)
Mn1-O1-Mn4	110.3(4)	121.4(5)	121.7(4)	117.6(4)	118.6(2)	121.8(2)
Mn2-O4-Mn4	109.4(4)	121.0(5)	120.9(4)	118.5(4)	118.3(2)	122.4(2)
Mn3-O7-Mn4	113.7(5)	124.4(5)	123.3(4)	119.8(4)	118.3(2)	122.7(2)
Mn1-O2-Na	111.0(4)	106.1(4)	106.3(4)	109.4(4)	108.6(2)	107.2(2)
Mn2-O5-Na	109.8(4)	107.6(4)	108.9(4)	108.1(4)	108.7(2)	117.2(6)
Mn3-O8-Na	107.9(4)	104.8(4)	109.3(4)	108.7(4)	108.4(2)	107.0(2)

Table S4. Selected bond distances (Å) and angles (°) for compounds **2*R*** and **2*S***.

d Å	(**2**-***R***)	(**2-S**)
Mn1-O1	1.893(6)	1.852(8)
Mn1-O2	1.903(6)	1.894(7)
Mn1-O7	1.881(1)	1.882(2)
Mn1-N1	1.979(6)	1.984(7)
Mn1-Cl1	2.601(2)	2.581(3)
Mn1-Cl1'	2.686(2)	2.711(3)
Mn2-O4	1.887(6)	1.894(8)
Mn2-O5	1.911(6)	1.880(8)
Mn2-O8	1.880(1)	1.879(2)
Mn2-N2	1.981(6)	1.968(7)
Mn2-Cl2	2.648(2)	2.665(3)
Mn2-Cl2'	2.717(2)	2.730(3)
Mn3-O1	2.214(5)	2.207(7)
Mn3-O4	2.195(5)	2.196(7)
Mn1-O1-Mn3	122.5(3)	123.4(3)
Mn2-O4-Mn3	125.5(3)	126.1(3)
Mn1-O7-Mn1'	119.51(7)	119.56(9)
Mn2-O8-Mn2'	118.8(1)	119.1(1)
Mn1-O2-Na1	107.0(3)	108.4(3)
Mn2-O5-Na2	108.1(3)	107.9(3)

Table S5. Selected bond distances (Å) and angles (°) for compound **3*R***.

Mn1-O1	1.881(3)	Mn5-O13	1.888(3)
Mn1-O2	1.908(3)	Mn5-O14	1.904(3)
Mn1-O19	1.882(3)	Mn5-O20	1.887(3)
Mn1-N1	1.998(3)	Mn5-N5	1.985(3)
Mn1-Br1	2.8328(7)	Mn5-Br4	2.8059(7)
Mn1-Br2	2.8271(7)	Mn5-Br5	2.8003(7)
Mn2-O4	1.891(3)	Mn6-O16	1.885(3)
Mn2-O5	1.912(3)	Mn6-O17	1.910(3)
Mn2-O19	1.885(3)	Mn6-O20	1.878(3)
Mn2-N2	1.980(3)	Mn6-N014	1.992(3)
Mn2-Br2	2.8023(7)	Mn6-Br5	2.8312(7)
Mn2-Br3	2.8005(7)	Mn6-Br6	2.7905(7)
Mn3-O7	1.891(3)	Mn7-O1	2.200(3)
Mn3-O8	1.903(3)	Mn7-O4	2.189(3)
Mn3-O19	1.885(3)	Mn7-O7	2.209(3)
Mn3-N3	1.985(3)	Mn7-O10	2.215(3)
Mn3- Br1	2.8457(7)	Mn7-O13	2.190(3)
Mn3-Br3	2.7937(7)	Mn7-O16	2.195(3)
Mn4-O10	1.884(3)		
Mn4-O11	1.911(3)		
Mn4-O20	1.888(3)		
Mn4-N4	1.987(3)		
Mn4-Br4	2.8145(7)		
Mn4-Br6	2.8808(7)		
Mn1-O1-Mn7	127.6(1)	Mn1-O19-Mn2	118.56(14)
Mn2-O4-Mn7	127.6(1)	Mn1-O19-Mn3	120.03(14)
Mn3-O7-Mn7	126.3(1)	Mn2-O(19-Mn3	117.83(13)
Mn4-O10-Mn7	128.2(1)	Mn4-O20-Mn5	118.0(1)
Mn5-O13-Mn7	127.7(1)	Mn4-O20-Mn6	120.3(1)
Mn6-O16-Mn7	127.9(1)	Mn5-O20-Mn6	117.3(1)

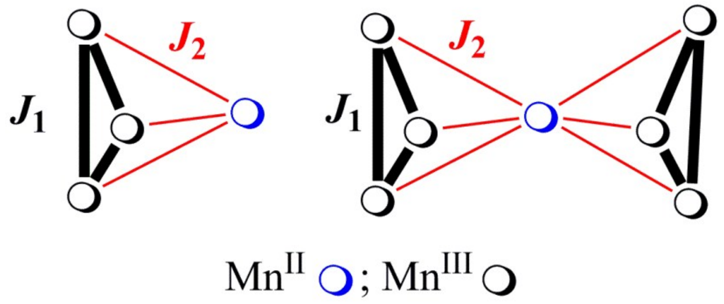

Fig. S3 Coupling scheme for complexes **1** (left), **2** and **3** (right). The derived Hamiltonians are :

$H = -2J_1(S_1 \cdot S_2 + S_1 \cdot S_3 + S_2 \cdot S_3) - 2J_2(S_1 \cdot S_4 + S_2 \cdot S_4 + S_3 \cdot S_4)$ for **1** and

$H = -2J_1(S_1 \cdot S_2 + S_1 \cdot S_3 + S_2 \cdot S_3 + S_4 \cdot S_5 + S_4 \cdot S_6 + S_5 \cdot S_6) - 2J_2(S_1 \cdot S_7 + S_2 \cdot S_7 + S_3 \cdot S_7 + S_4 \cdot S_7 + S_5 \cdot S_7 + S_6 \cdot S_7)$ for complexes **2** and **3**.

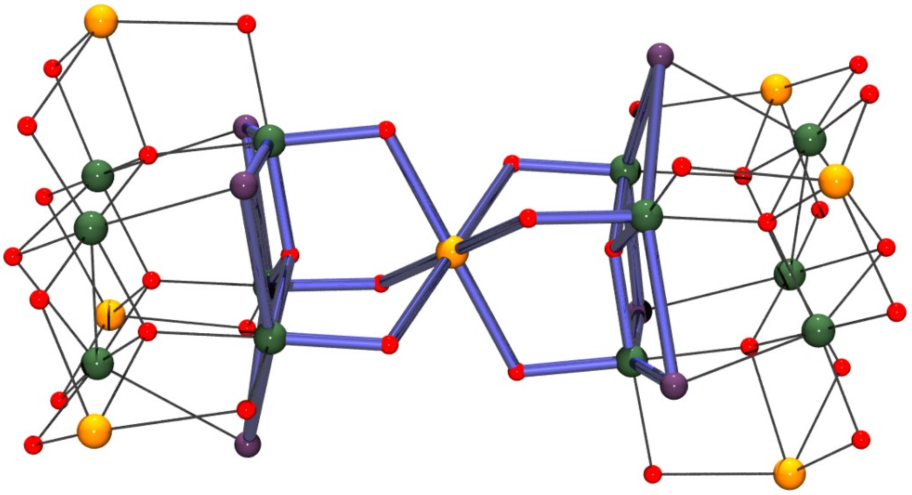

Fig. S4 Core of one typical $Mn^{III}{}_{12}Mn^{II}{}_7$ cluster[5]. The central $\{(\mu_3\text{-O})Mn^{III}{}_3\text{-}Mn^{II}\text{-}Mn^{III}{}_3(\mu_3\text{-O})\}$ fragment and in some case even the axial chloride ligands (enlighted as blue bonds) are equivalent to the core of complexes **2**-**3**. Note the out-of plane position of the μ_3-O donors, towards the central Mn^{II} cation.