Electronic Supplementary Information

A Homochiral Magnet Based on D_3 Symmetric $[(NaO_3)Co_3]$ Clusters: from Spontaneous Resolution to Absolute Chiral Induction

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Experimental Section

The reagents and solvents employed were commercially available and used without further purification. Elemental analyses were performed on a Vario EL-II elemental analyzer. The elemental composition of the samples was analyzed with energy-dispersive X-ray spectroscopy (EDX) attached to SEM instrument. The FTIR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Nicolet 5DX spectrometer. Powder X-ray diffraction (PXRD) data were collected in a Bruker D8 ADVANCE diffractometer ($Cu_{K\alpha}$, λ= 1.5418 Å). The thermogravimetric analysis (TGA) were carried out under air atmosphere using SETARAM LABSYS equipment at a heating rate of 10 °C/min. Circular dichroism (CD) experiments were performed on a Jasco J-815 circular dichroism spectrometer at room temperature. The magnetic measurements were made with Quantum Design SQUID MPMS XL-5 instruments. Data were corrected for the diamagnetic contribution calculated from Pascal constants and the sample container. Electron spin resonance (ESR) spectroscopy was performed on polycrystalline powder samples, using a Bruker Elexsys E-500 CW spectrometer at low temperature 77 K.

Synthesis of racemate (±)-$[NaCo_3(IA)_6](NO_3)\cdot H_2O$ (1) : A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.100 g, 0.40 mmol), HIA (0.055 g, 0.40 mmol), C_2H_5OH (5 mL) and H_2O (1 mL) was stirred and adjusted to pH = 6 by the dropwise addition of 2M NaOH solution, then sealed in a 15 mL Teflon-lined stainless autoclave at 180°C for 4 days. After it was cooled to room temperature and subjected to filtration, red hexagonal prism crystals of 1 in yield of 62.3% (based on IA) were recovered. Anal. calcd (%) for **$C_{36}H_{32}Co_3N_{13}NaO_{16}$ (1)**: C, 39.22; H, 2.93; N, 16.52. Found: C, 39.26; H, 2.99; N, 16.50. IR data (KBr, cm^{-1}): 3416(b), 3133(w), 2927(w), 1657(m), 1587(m), 1545(m), 1384(s), 1279(m), 1123(s),

970(m), 833(w), 695(w), 644(w).

Syntheses of enantiopure (+)-[$NaCo_3(IA)_6$](NO_3)·H_2O (1Δ) and (-)-[$NaCo_3(IA)_6$](NO_3)·H_2O (1Λ) : A procedure similar to **1** was employed to synthesize **1Δ** and **1Λ** except that *S*-(+)-mand or *R*-(-)-mand (0.015 g, 0.10 mmol) was added the reaction mixture. After it was cooled to room temperature and subjected to filtration, red hexagonal prism crystals of **1Δ** (69.6%) or **1Λ** (58.6%) was recovered, respectively. Anal. calcd (%) for $C_{36}H_{32}Co_3N_{13}NaO_{16}$: C, 39.22; H, 2.93; N, 16.52. Found for **1Δ**: C, 39.19; H, 2.97; N, 16.55; found for **1Λ**: C, 39.28; H, 2.90; N, 16.49, respectively.

Crystallography studies. Single crystal X-ray diffraction measurements were carried out on an Agilent Technologies Gemini Eos diffractometer at 298.15 K using Cu Kα radiation (λ = 0.15418 Å). The crystal structures of ten randomly picked crystals of **1** from the same reaction system have been investigated. The program SAINT was used for integration of the diffraction profiles, and the program SADABS was used for absorption correction. The structures were solved with XS by direct method and refined anisotropically by full-matrix least-squares technique based on F^2 using the Olex2 programs. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of organic ligand were generated theoretically onto the specific carbon and refined isotropically with fixed thermal factors. The crystallographic data are listed in Table S2, selected bond lengths and bond angles are given in Table S3.

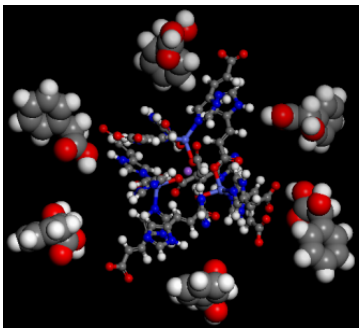


Figure S1. View of the the hydrogen bond interaction between IA and S-mand.

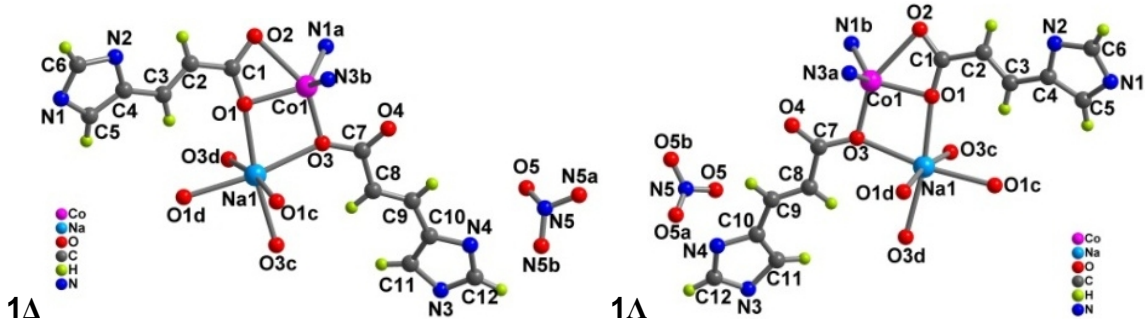


Figure S2. View of the coordination environment of cobalt atom and sodium atom in **1Δ** and **1Λ.**

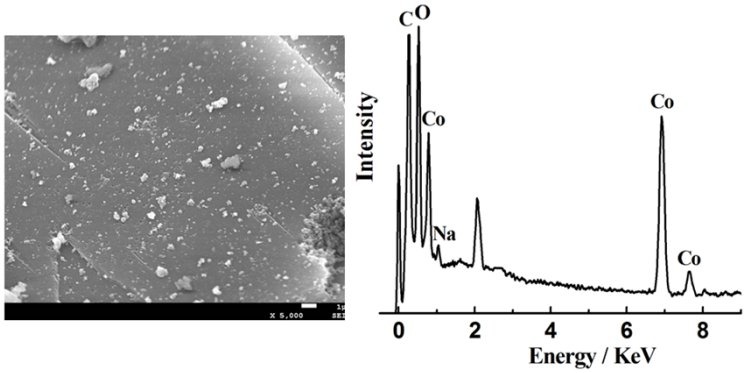


Figure S3. SEM and EDS of **1**.

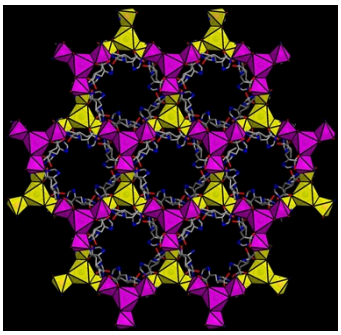


Figure S4. Polyhedral plot of the 3D structure for **1**.

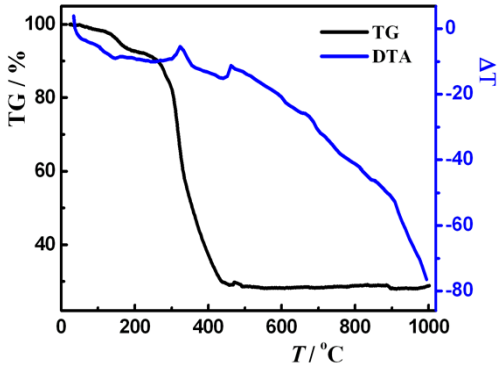


Figure S5. The TG/DTA plots of **1**.

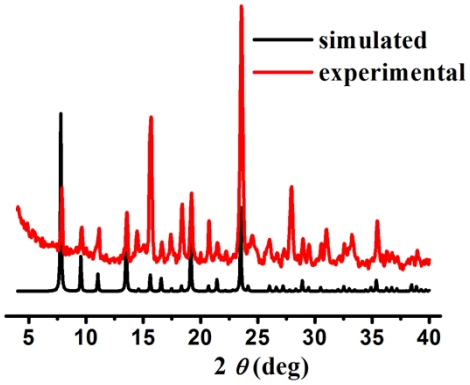


Figure S6. The PXRD patterns of simulated and experimental for **1**.

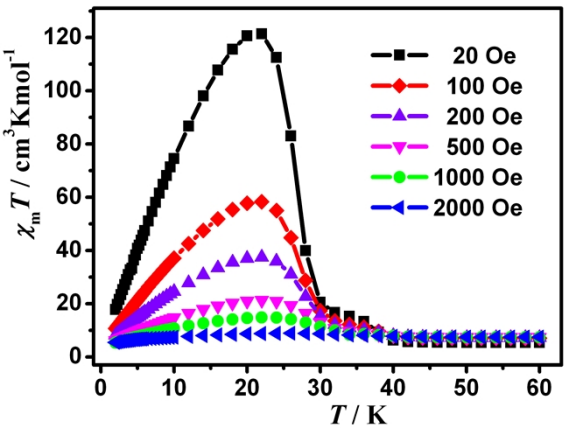
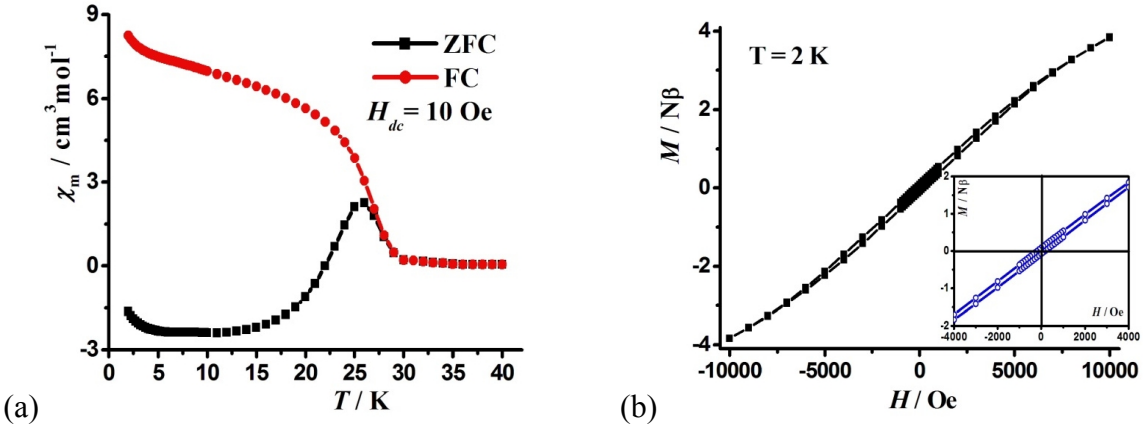


Figure S7. Temperature dependence of the susceptibility in different applied magnetic fields for **1.**



(a) (b)

Figure S8. (a) FC and ZFC magnetization at 10 Oe, and (b) the hysteresis loop at 2 K for **1**, inset: enlargement plot.

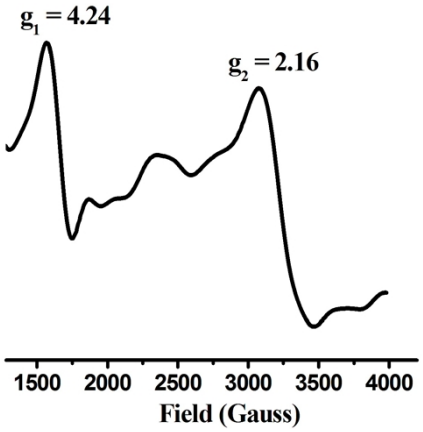


Figure S9. X-band ESR spectra of **1** measured at low temperature 77 K.

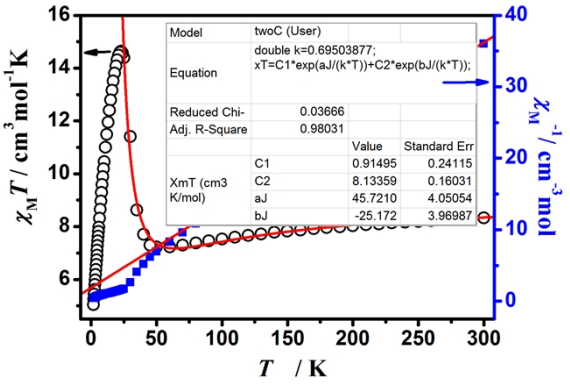


Figure S10. The $\chi_m T$ versus T plots for **1**, the red solid line represents the best fit given in the text. Inset: the table of fit parameters.

Table S1: A summary of the crystal data and refinement results for 10 randomly selected crystals of **1** with space group $P6_3$.

	a	c	R_1	wR_2	Flack
1	13.1653(8)	16.0623(12)	0.0691	0.1206	-0.06(4)
2	13.1210(3)	16.0099(4)	0.0503	0.1392	-0.009(7)
3	13.1191(3)	16.0140(5)	0.0440	0.1074	-0.006(10)
4	13.1178(3)	16.0292(4)	0.0406	0.1096	-0.016(7)
5	13.1187(4)	16.0068(5)	0.0394	0.1031	0.038(7)
6	13.1141(4)	16.0140(7)	0.0497	0.1216	-0.031(11)
7	13.1181(4)	16.0072(6)	0.0419	0.1127	0.010(7)
8	13.1112(4)	16.0170(5)	0.0565	0.1570	0.006(9)
9	13.1118(4)	16.0223(6)	0.0621	0.1705	0.018(9)
10	13.1177(4)	16.0050(4)	0.0454	0.1215	0.001(6)

Note: 1-3 with **Λ** configuration, 4-10 with **Δ** configuration.

Table S2. Crystal data and refinement parameters for compounds **1Δ** and **1Λ**

Compound	**1Δ**	**1Λ**
Empirical formula	$C_{36}H_{32}Co_3N_{13}NaO_{16}$	$C_{36}H_{32}Co_3N_{13}NaO_{16}$
Formula weight	1102.51	1102.51
Crystal system	hexagonal	hexagonal
Space group	***P6₃***	***P6₃***
a (Å)	13.1178(3)	13.1653(8)

b (Å)	13.1178(3)	13.1653(8)
c (Å)	16.0292(4)	16.0623(12)
α(°)	90	90
β (°)	90	90
γ(°)	120	120
V (Å^3)	2388.72(12)	2411.0(3)
Z	2	2
$\rho_{calc,}$(mg cm^{-3})	1.508	1.516
μ (mm^{-1})	8.825	1.108
F(000)	1098.0	1114.0
Crystal size (mm)	0.28× 0.25 × 0.22	0.28 × 0.26 × 0.23
Reflections	4597	5337
R_{int}	0.0344	0.0704
Data/parameters	1864/210	2716/218
S	1.133	0.992
R_1[a], wR_2 [b][$I > 2(I)$]	0.0406, 0.1096	0.0691, 0.1206
R_1,wR_2 (all data)	0.0422, 0.1118	0.1067, 0.1428
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (eÅ^{-3})	0.90/-0.29	0.87/-0.46
Flack parameter	-0.016(7)	-0.06(4)

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, b. $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S3. Selected bond length and bond angle for compounds **1Δ** and **1Λ**

Compound 1Δ			
Na(1)-O(1)	2.371(7)	Co(1)-O(1)	2.054(6)
Na(1)-O(1c)	2.371(7)	Co(1)-O(2)	2.344(6)
Na(1)-O(1d)	2.371(7)	Co(1)-O(3)	2.019(5)
Na(1)-O(3)	2.381(7)	Co(1)-N(1a)	2.027(7)
Na(1)-O(3c)	2.381(7)	Co(1)-N(3b)	2.029(8)
Na(1)-O(3d)	2.381(7)	Co(1)-Na(1)	3.2814(8)
O(3)-Co(1)-O(1)	92.03(18)	N(1a)-Co(1)-O(1)	123.2(3)

O(3)-Co(1)-O(2)	150.5(3)	N(1a)-Co(1)-O(2)	87.3(2)
O(3)-Co(1)-N(1a)	104.1(3)	N(1a)-Co(1)-N(3b)	119.0(3)
O(3)-Co(1)-N (3b)	110.5(3)	N(3b)-Co(1)-O(1)	104.4(3)
O(1)-Co(1)-O(2)	59.6(3)	N(3b)-Co(1)-O(2)	86.3(3)
O(3c)-Na(1)-O(3)	96.4(3)	O(1)-Na(1)-O(1d)	98.3(3)
O(3)-Na(1)-O(3d)	96.4(3)	O(1c)-Na(1)-O(1d)	98.3(3)
O(3c)-Na(1)-O(3d)	96.4(3)	O(1)-Na(1)-O(1c)	98.3(3)
O(3d)-Na(1)-O(1d)	76.13(15)	O(1)-Na(1)-O(3c)	170.81(18)
O(3)-Na(1)-O(1d)	170.81(18)	O(1)-Na(1)-O(3d)	89.82(18)
O(3c)-Na(1)-O(1d)	89.82(18)	O(1)-Na(1)-O(3)	76.14(15)
O(3)-Na(1)-O(1c)	89.82(17)	O(1c)-Na(1)-O(3d)	170.81(18)
O(3c)-Na(1)-O(1c)	76.13(15)		

Symmetry codes: (a) +y,-x+y,1/2+z; (b) -y+x,1+x,-1/2+z; (c) -1-y,+x-y,+z; (d) -1+y-x,-1-x,+z

Compound 1Λ

Na(1)-O(1)	2.371(15)	Co(1)-O(1)	2.065(15)
Na(1)-O(1e)	2.371(15)	Co(1)-O(2)	2.337(13)
Na(1)-O(1f)	2.371(15)	Co(1)-O(3)	2.047(13)
Na(1)-O(3)	2.389(14)	Co(1)-N(1a)	2.067(16)
Na(1)-O(3e)	2.389(14)	Co(1)-N(3b)	1.99(2)
Na(1)-O(3f)	2.389(14)	Co(1)-Na(1)	3.2929(15)
N(1a)-Co(1)-O(2)	87.1(5)	O(1)-Co(1)-N(3b)	103.8(7)
N(3b)-Co(1)-O(3)	111.6(8)	O(3)-Co(1)-O(2)	150.3(6)
N(3b)-Co(1)-N(1a)	119.4(7)	N(1a)-Co(1)-O(3)	104.1(6)
O(3)-Co(1)-O(1)	91.9(4)	N(3b)-Co(1)-O(2)	85.0(7)
N(1a)-Co(1)-O(1)	122.6(7)	O(2)-Co(1)-O(1)	59.5(6)
O(1e)-Na(1)-O(1f)	97.5(5)	O(3f)-Na(1)-O(1e)	90.1(3)
O(1e)-Na(1)-O(1)	97.5(5)	O(1e)-Na(1)-O(3e)	76.7(3)
O(1f)-Na(1)-O(1)	97.5(5)	O(3)-Na(1)-O(1f)	90.1(3)
O(3)-Na(1)-O(1e)	171.0(3)	O(3f)-Na(1)-O(1f)	76.7(3)
O(3e)-Na(1)-O(1f)	171.0(3)	O(1)-Na(1)-O(3)	76.7(3)

O(3f)-Na(1)-O(1)	171.0(3)	O(3e)-Na(1)-O(1)	90.1(3)
O(3f)-Na(1)-O(3)	96.3(5)	O(3e)-Na(1)-O(3f)	96.3(5)
O(3e)-Na(1)-O(3)	96.3(5)		

Symmetry codes: (a) +y,1-x+y,-1/2+z; (b) -y+x,+x,1/2+z; (c) 1-y+x,+x,1/2+z;
(d) +y,-x+y,-1/2+z; (e)1+y-x,1-x,+z; (f)1-y,+x-y,+z