Supporting Information

Crystal Structure, Assembly Process, and Single-Molecule Magnet Behavior of A Triangular Prismatic $\{Co_9\}$ Cluster

Ye Tao,[a] Lu-Na Wang, [a] Hai-Ye Li, [a] Xiao-Huan Qin, [a] Di Yao, [a] and Fu-Ping Huang [*,a]

[a] State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin 541004, P. R. China. E-mail: huangfp2010@163.com;

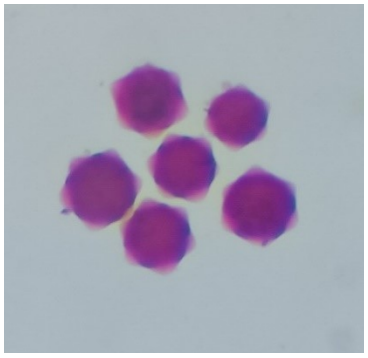


Fig. S1 The crystal photograph of **{Co$_9$}-Eg.**

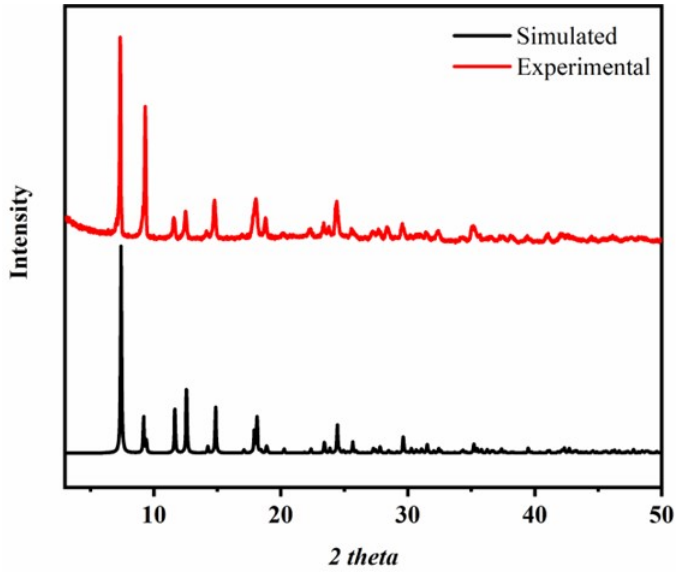


Fig. S2 Powdered X-ray diffraction (XRD) patterns of **{Co$_9$}-Eg.**

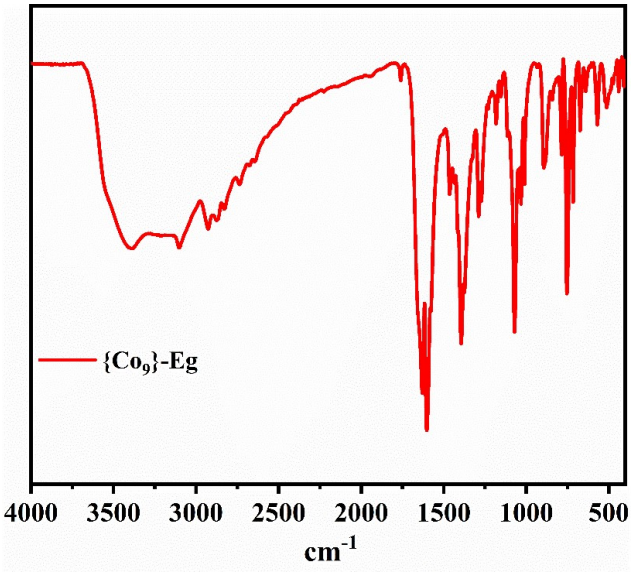


Fig. S3 Fourier transform Infrared (FT-IR) spectrum of **{Co$_9$}-Eg.**

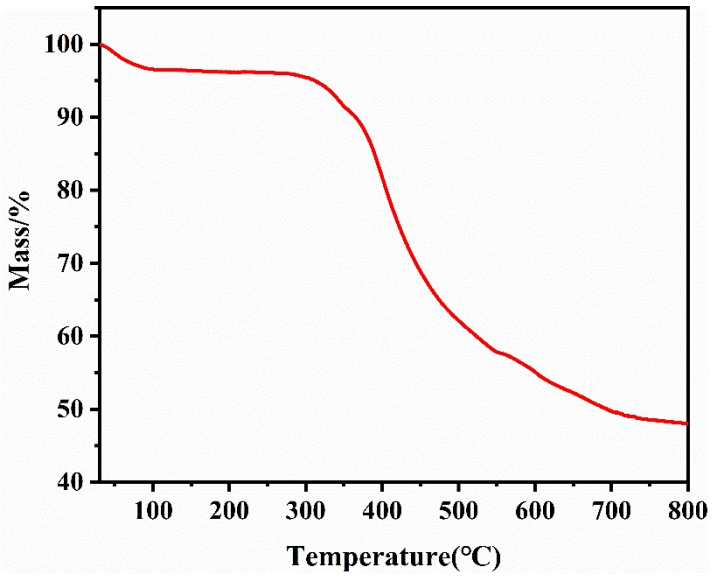


Fig. S4 The TGA plot of **{Co_9}-Eg**.

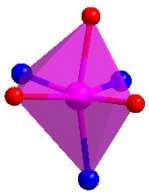
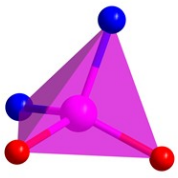
Table S1. Crystallographic data and refinement parameters for **{Co_9}-Eg** (squeeze)**.**

Identification code	**{Co_9}-Eg**
Empirical formula	$Co_9C_{60}H_{48}N_{24}O_{24}$
Formula weight (M)	2019.55
Crystal system	trigonal
Space group	*R-3c*
a (Å)	15.1762(6)
b (Å)	15.1762(6)
c (Å)	56.387(4)
α (°)	90
β (°)	90
γ (°)	120
V/(Å3)	11246.9(13)
Z	6
Dc (Mg m^{-3})	1.789
F(000)	6066
Reflections collected	16568/3039
/unique	R(int) = 0.0655
Goodness-of-fit on F2	1.010
Final R indices	R_1 = 0.0681
I > 2σ(I)	ωR_2 = 0.1824
R indices	R_1 = 0.1324
(all data)	ωR_2 = 0.2355

Table S2. Selected bond length and bond angle for **{Co$_9$}-Eg.**

{Co$_9$}-Eg. (A) -*y*+1, *x*-*y*, *z*; (B) -*x*+4/3, -*x*+*y*+2/3, -*z*+1/6; (C) *y*+1/3, *x*-1/3, -*z*+1/6;			
Atomic Distances [Å]			
Co1—O1	2.079 (5)	Co1—N3A	2.263 (5)
Co1—O3	1.947 (4)	Co2—O3	1.886 (4)
Co1—O4	2.168 (7)	Co2—O3B	1.885 (4)
Co1—N1	2.043 (5)	Co2—N4C	1.998 (5)
Co1—N2	2.403 (5)	Co2—N4A	1.998 (5)
Bond Angles [°]			
O1—Co1—O4	88.8 (2)	N1—Co1—O4	89.4 (2)
O1—Co1—N2	152.66 (19)	N1—Co1—N2	74.9 (2)
O1—Co1—N3A	103.91 (19)	N1—Co1—N3A	101.4 (2)
O3—Co1—O1	103.81 (19)	N3i—Co1—N2	83.25 (18)
O3—Co1—O4	80.0 (2)	O3—Co2—O3B	111.6 (3)
O3—Co1—N1	169.3 (2)	O3—Co2—N4A	99.06 (19)
O3—Co1—N2	102.70 (19)	O3—Co2—N4C	124.0 (2)
O3—Co1—N3A	88.58 (19)	O3B—Co2—N4C	99.06 (19)
O4—Co1—N2	89.3 (2)	O3B—Co2—N4A	124.0 (2)
O4—Co1—N3A	164.7 (2)	N4A—Co2—N4C	100.8 (3)
N1—Co1—O1	77.8 (2)		

Table S3. Continuous Shape Measures (CShM) for Co^{II} centres using SHAPE.

	Co1	Co2
	[CoN3O3]	[CoN2O2]
{Co$_9$}-Eg		
	octahedron	tetrahedron
	2.755	1.818

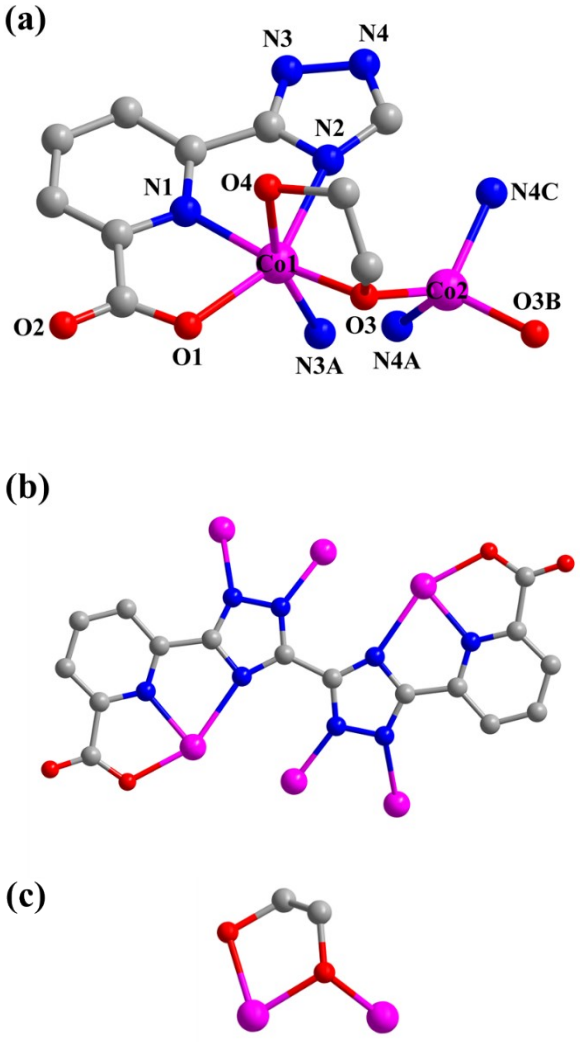


Fig. S5 (a) Coordination environment diagram of **{Co_9}-Eg.** Coordination modes of ligands L^{4-} **(b)** and EgO_2H^- **(c)**.

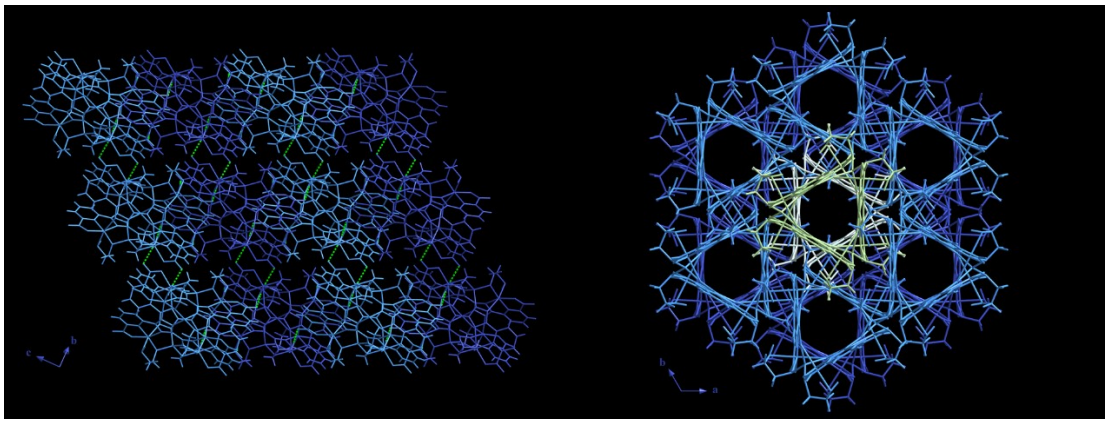


Fig. S6 The packing arrangement of **{Co_9}-Eg** along the a-(left) and c-axis (right) directions, respectively.

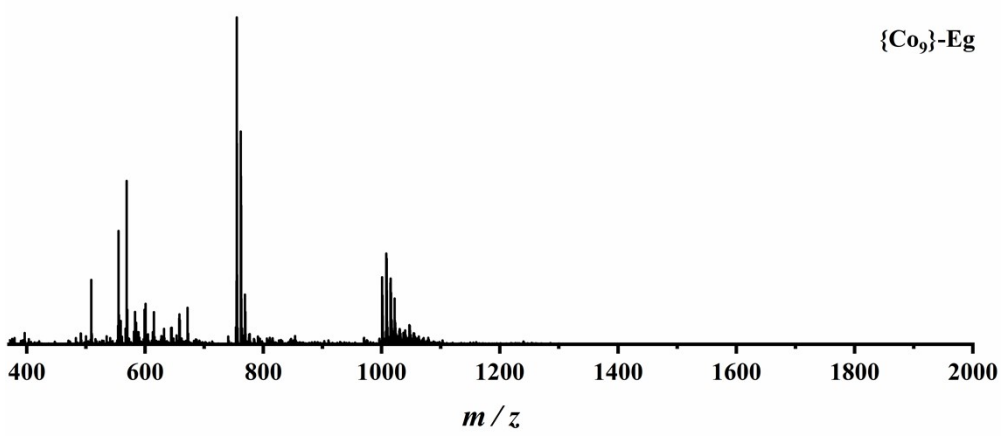


Fig. S7 Negative ESI-MS spectra of **{Co$_9$}-Eg** in H_2O (In-Source CID = 0 eV).

Table S4. Major species assigned in the ESI-MS in Negative mode.

{Co$_9$}-Eg (In-Source CID 0 eV)			
Peaks	Relative Intensity		
Typical Composition	Intensity	Observed *m/z*	Calculated *m/z*
$[Co_2L(OH)]^-$	0.20	508.92	508.92
$[Co_2L(OH)(HCOOH)]^-$	0.35	554.92	554.93
$[Co_2L(CH_3O)(HCOOH)]^-$	0.50	568.94	568.94
$[Co_2L(HCOO)(HCOOH)]^-$	0.10	582.92	582.92
$[Co_2L(HCOO)(HCOOH)(H_2O)]^-$	0.12	600.93	600.93
$[Co_3L(HCOO)(CH_3O)(OH)]^-$	0.05	643.87	643.87
$[Co_3L(HCOO)_2(OH)]^-$	0.09	657.84	657.85
$[Co_3L(HCOO)_2(CH_3O)]^-$	0.11	671.86	671.86
$[Co_6L_3(OH)_2]^{2-}$	1	754.87	754.87
$[Co_6L_3(OH)(CH_3O)]^{2-}$	0.65	761.88	761.88
$[Co_6L_3(CH_3O)_2]^{2-}$	0.15	768.89	768.89
$[Co_9L_3(EgO_2H)_5(OH)(CH_3O)\text{-}H]^{2-}$	0.20	1002.34	1002.35
$[Co_9L_3(EgO_2H)_6\text{-}2H]^{2-}$	0.28	1008.35	1008.35
$[Co_9L_3(EgO_2H)_5(CH_3O)(HCOO)\text{-}H]^{2-}$	0.20	1016.34	1016.35
$[Co_9L_3(EgO_2H)_5(HCOO)_2\text{-}H]^{2-}$	0.14	1023.34	1023.34

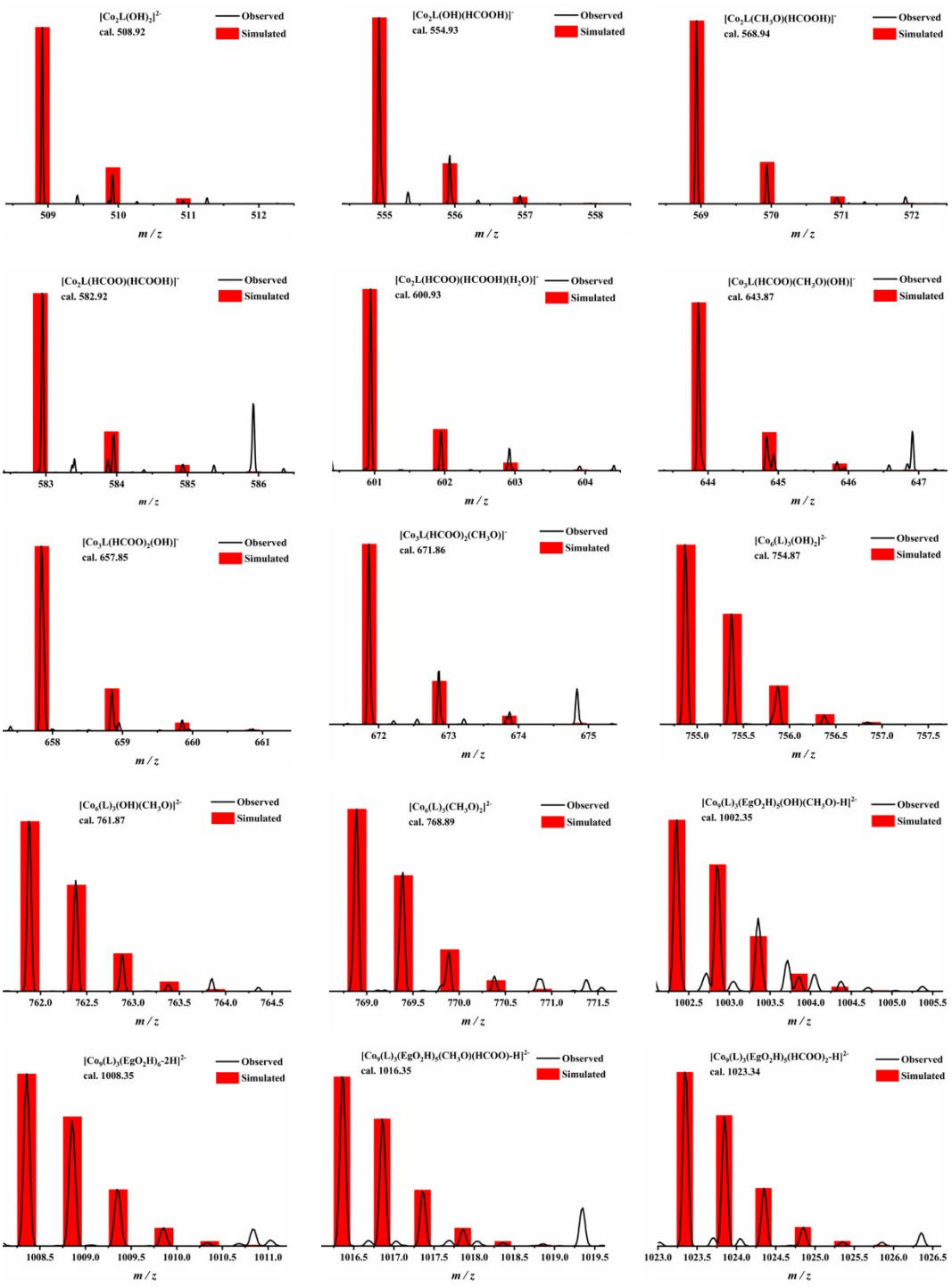


Fig. S8 The superposed simulated and observed spectra of ESI-MS species for **{Co$_9$}-Eg** in negative mode (In-Source CID = 0 eV).

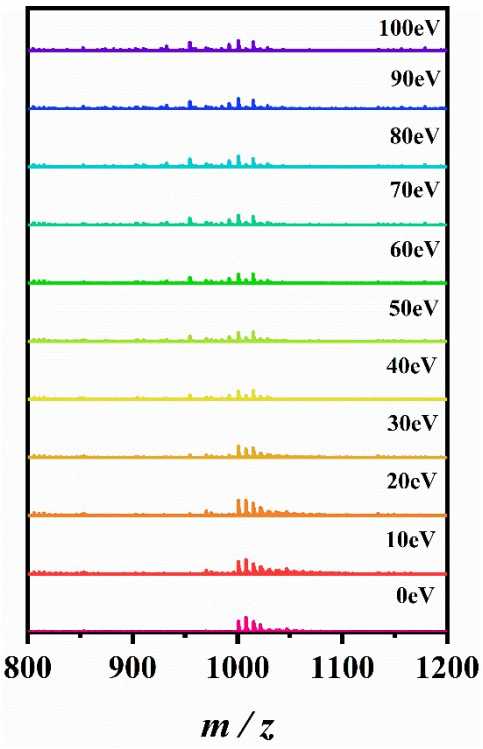
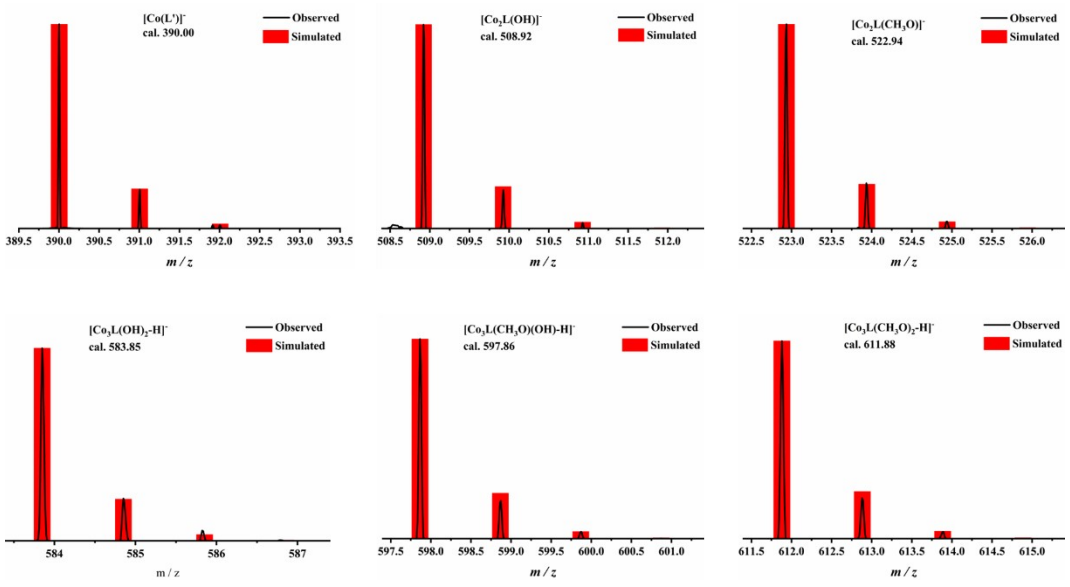


Fig. S9 Ion peaks of **{Co$_9$}-Eg** in anion modes obtained by ESI-MS test with different ion source voltages (0-100 eV).

Table S5. Time-dependent ESI-MS spectra assigned in the HRESI-MS of **{Co$_9$}-Eg** in negative mode.

	m/z	Fragment	Relative Intensity					
			5 min	15 min	30 min	1 h	2 h	4 h
CoL	390.00	$[CoL']^-$ Cal. 390.00	0.15	0.20	0.11	0.05	0.04	0.04
Co_2L	508.92	$[Co_2L(OH)]^-$ Cal. 508.92	0.41	0.38	0.22	0.18	0.18	0.16
	522.93	$[Co_2L(CH_3O)]^-$ Cal. 522.94	1	1	1	1	1	1
Co_3L	583.85	$[Co_3L(OH)_2\text{-}H]^-$ Cal. 583.85	0.02	0.05	0.05	0.03	0	0
	597.86	$[Co_3L(CH_3O)(OH)\text{-}H]^-$ Cal. 597.86	0.07	0.10	0.20	0.11	0	0
	611.88	$[Co_3L(CH_3O)_2\text{-}H]^-$ Cal. 611.88	0.10	0.18	0.28	0.17	0.04	0.06
Co_5L_2	1107.79	$[Co_5L_2(CH_3O)(OH)_2]^-$ Cal. 1107.79	0	0	0	0.06	0.04	0.03
	1135.82	$[Co_5L_2(CH_3O)_3]^-$ Cal. 1135.82	0	0	0.05	0.20	0.11	0.08
Co_6L_3	807.91	$[Co_6L_3(EgO_2H)_2(H_2O)]^{2-}$ Cal. 807.91	0	0	0	0.06	0.12	0.07

	814.92	$[Co_6L_3(EgO_2H)_2(CH_3OH)]^{2-}$ Cal. 814.92	0	0	0	0.18	0.09	0.06
	1616.83	$[Co_6L_3(EgO_2H_2)_2(H_2O)\text{-}H]^{-}$ Cal. 1616.83	0	0	0	0.04	0.03	0
	1630.84	$[Co_6L_3(EgO_2H_2)_2(CH_3OH)\text{-}H]^{-}$ Cal. 1630.84	0	0	0	0.20	0.10	0.11
	1705.91	$[Co_6L_3(EgO_2H_2)_3(Me_2NH)\text{-}H]^{-}$ Cal. 1705.91	0	0	0	0.12	0.07	0.07
Co_7L_3	874.40	$[Co_7L_3(EgO_2H)_3(CH_3O)]^{2-}$ Cal. 874.40	0	0	0	0	0.03	0.07
Co_9L_3	1002.35	$[Co_9L_3(EgO_2H)_5(OH)(CH_3O)\text{-}H]^{2-}$ Cal. 1002.35	0	0	0	0	0.04	0.10
	1008.35	$[Co_9L_3(EgO_2H)_6\text{-}2H]^{2-}$ Cal. 1008.35	0	0	0	0	0.08	0.14
	1030.88	$[Co_9L_3(EgO_2H)_6(Me_2NH)\text{-}2H]^{2-}$ Cal. 1030.88	0	0	0	0	0.06	0.07



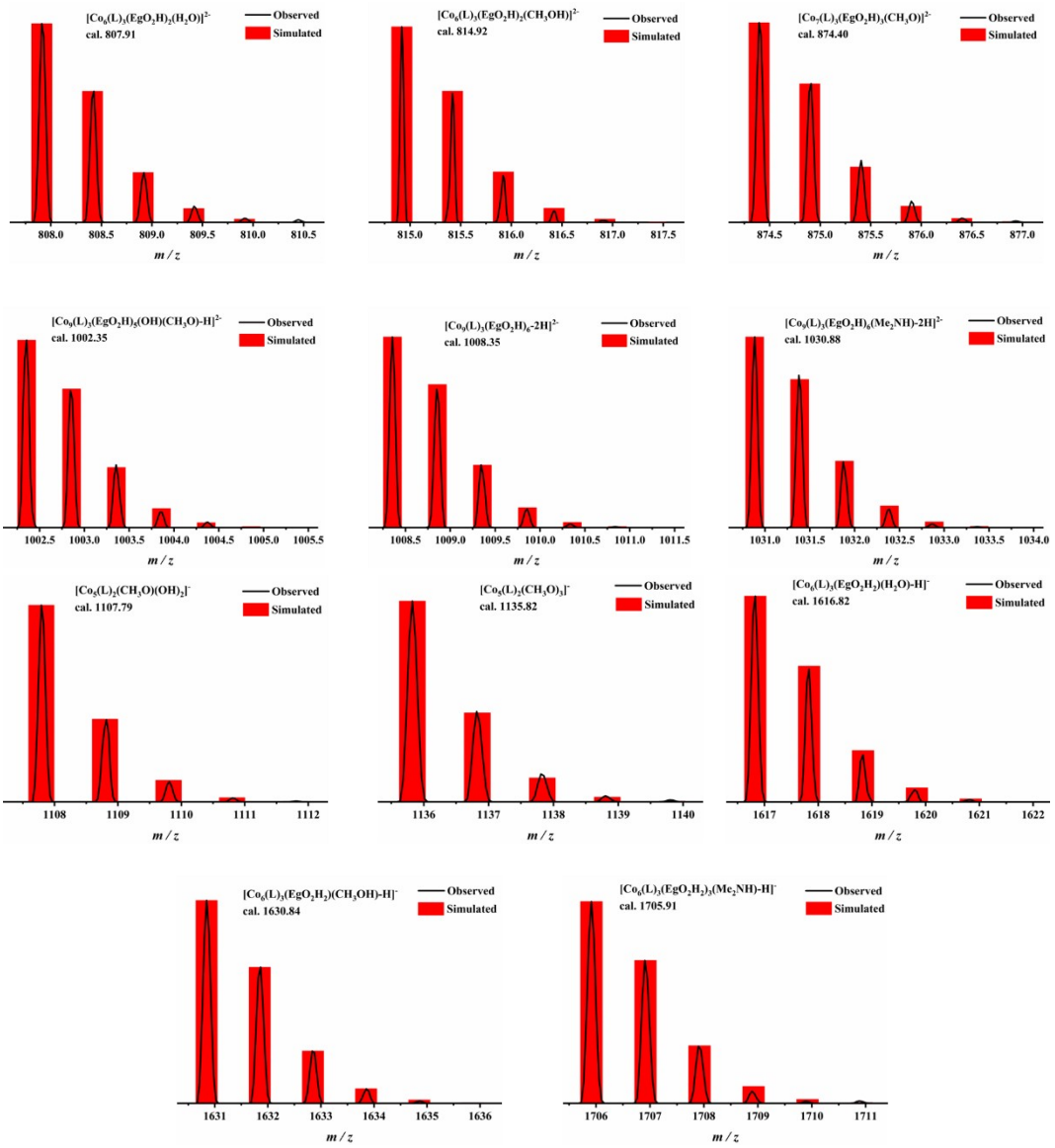


Fig. S10 The superposed simulated and observed spectra of time-dependent ESI-MS species for **{Co$_9$}-Eg** in negative mode.

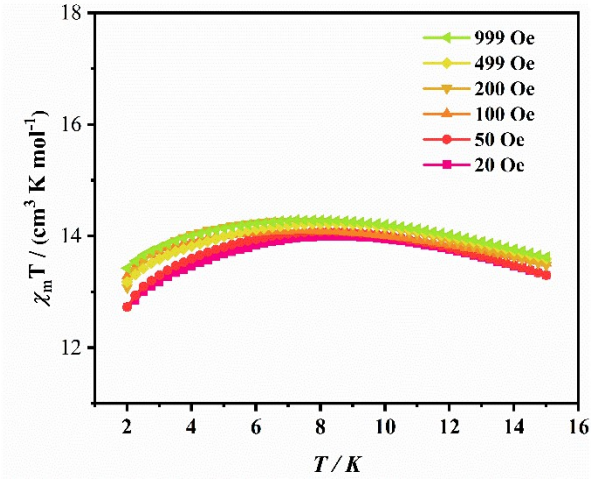


Fig. S11 The field-cold susceptibility from 2 to 15 K at different magnetic fields.

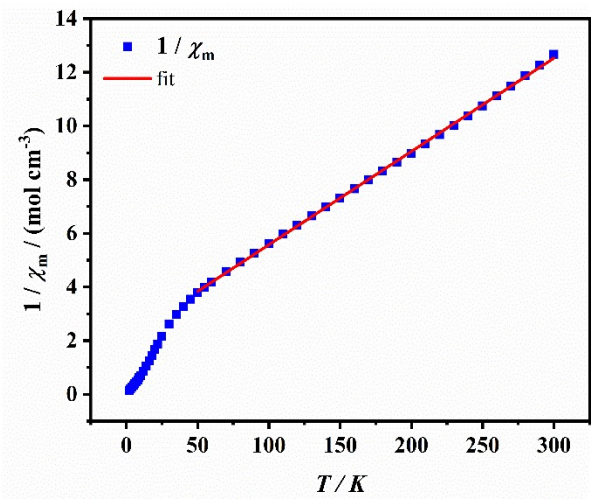


Fig. S12 Calculated (red solid line) and experimental (blue square dot) data of $1/\chi_M$ of **{Co$_9$}-Eg**.

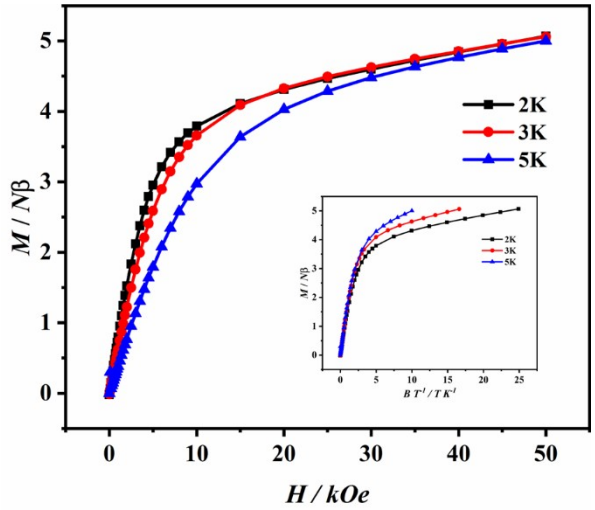


Fig. S13. Field dependence of magnetization for **{Co$_9$}-Eg**. Inset: M versus H/T plot for **{Co$_9$}-Eg**.

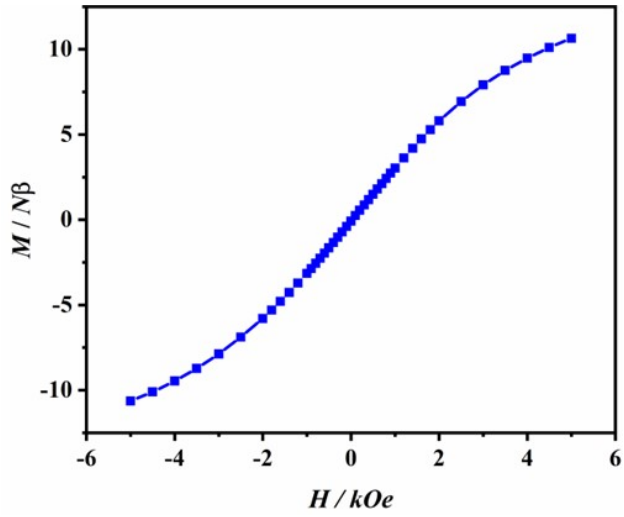


Fig S14. Variable magnetic field magnetization measurement for **{Co$_9$}-Eg** at 2 K.

Table S6. Best fit parameters of the generalized Debye model at temperature ranging from 2 to 5 K under a 0 Oe DC field for **{Co_9}-Eg**. χ_T stands for the isothermal susceptibility, χ_S for the adiabatic susceptibility, α for the relaxation time, and τ accounts for the distribution width of the relaxation time.

	χ_S / $cm^3mol^{-1}K$	χ_T / $cm^3mol^{-1}K$	τ / s	α
2.0	0.71464	4.77452	0.00164	0.45234
2.3	0.65316	4.17136	0.0016	0.44468
2.6	0.63446	3.70872	0.00153	0.42442
2.9	0.6736	3.31546	0.00134	0.36403
3.2	0.69055	2.9846	9.2461E-4	0.27992
3.5	0.67746	2.71826	5.30826E-4	0.20821
3.8	0.67763	2.50096	2.85496E-4	0.15523
4.1	0.7078	2.31939	1.56076E-4	0.11502
4.4	0.73099	2.15968	8.64443E-5	0.07967
4.7	0.83374	2.03059	5.34317E-5	0.04784
5.0	0.94051	1.91396	3.40955E-5	0.02379

Squeeze results for {Co_9}-Eg is as follows:

loop_
_platon_squeeze_void_nr
_platon_squeeze_void_average_x
_platon_squeeze_void_average_y
_platon_squeeze_void_average_z
_platon_squeeze_void_volume
_platon_squeeze_void_count_electrons
_platon_squeeze_void_content

1	0.000	0.000	0.000	72	15 ''
2	0.000	0.000	0.097	36	3 ''
3	0.000	0.444	0.250	11	5 ''
4	0.000	0.000	0.403	36	3 ''
5	0.000	0.000	0.500	72	15 ''
6	0.000	0.000	0.597	36	3 ''
7	0.000	0.556	0.750	11	5 ''
8	0.000	0.000	0.903	36	3 ''
9	0.111	0.778	0.083	9	5 ''
10	0.111	0.333	0.583	9	5 ''
11	0.222	0.333	0.083	9	5 ''
12	0.333	0.667	0.167	73	16 ''
13	0.222	0.889	0.583	9	5 ''
14	0.333	0.667	0.667	73	15 ''
15	0.333	0.667	0.263	35	3 ''
16	0.333	0.667	0.763	35	3 ''
17	0.333	0.667	0.070	35	3 ''

18	0.333	0.667	0.570	35	3 ''
19	0.333	0.222	0.417	9	5 ''
20	0.333	0.111	0.917	9	5 ''
21	0.444	1.000	0.250	11	5 ''
22	0.444	0.444	0.750	11	5 ''
23	0.555	0.556	0.250	11	5 ''
24	0.667	0.333	0.333	72	15 ''
25	0.555	0.000	0.750	11	5 ''
26	0.667	0.333	0.833	72	15 ''
27	0.667	0.333	0.430	35	3 ''
28	0.667	0.333	0.930	35	3 ''
29	0.667	0.333	0.237	35	3 ''
30	0.667	0.333	0.737	35	3 ''
31	0.667	0.889	0.083	10	5 ''
32	0.667	0.778	0.583	10	5 ''
33	0.778	0.111	0.417	9	5 ''
34	0.778	0.667	0.917	10	5 ''
35	0.889	0.667	0.417	10	5 ''
36	0.889	0.222	0.917	9	5 ''

That is, SQUEEZE gives 217 electrons/unit cell for the voids. If these electrons are all from H_2O ($10e^-$), each unit cell has $217/10 \approx 22$ H_2O molecules, and each formula unit has 3.5 H_2O molecules (since Z = 6). So the suitable formula for this compound should be **$[Co_9L_3(CH_2OCH_2OH)_6]\cdot 3.5H_2O$**