Supporting Informations

A Multifaceted Cage Cluster, $[Co^{II}_6O_{12} \supset X]^-$ (X = Cl^- or F^-): Halide Template Effect and Frustrated Magnetism

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Table S1. Selected bond lengths (Å) and angles (°) for **1**, **2** and **1′.**

1					
Co1-N1	2.142(5)	O1A-Co1-N1	97.97(2)	O3B-Co1-N2	98.63(2)
Co1-N2	2.149(4)	O1A-Co1-N2	99.05(2)	O3B-Co1-O1	87.22(1)
Co1-O1	2.387(3)	O1A-Co1-O3B	157.01(1)	O1A-Co1-O1	86.92(2)
Co1-O3	2.400(3)	O1-Co1-N1	69.17(1)	O1-Co1-N2	144.44(2)
Co1-O1A	2.054(4)	O3B-Co1-O3	86.59(5)	O1A-Co1-O3	86.17(14)
Co1-O3B	2.059(4)	O1A-Co1-Cl	78.41(9)	O1-Co1-Cl	73.31(9)
Co1-Cl	2.7023(8)	N1-Co1-N2	75.27(2)	O3-Co1-Cl	73.33(9)
N1-Co1-O3	144.16(1)	O3B-Co1-N1	100.65(2)	N1-Co1-Cl	142.46(1)
N2-Co1-O3	68.93(2)	O3B-Co1-Cl	78.61(9)	N2-Co1-Cl	142.26(1)
2					
Co1-N1	2.1403(9)	O3D-Co1-O1C	155.93(3)	O1C-Co1-O3	86.75(2)
Co1-N2	2.1470(7)	O3D-Co1-N2	98.71(3)	N2-Co1-O3	70.03(3)
Co1-O1	2.3498(6)	O1C-Co1-N2	100.94(3)	N1-Co1-O3	144.25(2)
Co1-O3	2.3483(7)	O1C-Co1-N1	99.17(2)	O3D-Co1-O1	86.04(2)
Co1-O1C	2.0424(6)	N2-Co1-N1	74.24(3)	O1C-Co1-O1	86.281(1)
Co1-O3D	2.0229(7)	O3D-Co1-O3	87.04(2)	N2-Co1-O1	143.77(3)
N1-Co1-O1	69.56(3)	O3-Co1-O1	146.19(2)		
1′					
Co1-N1	2.122(2)	O3E-Co1-N2	97.3(8)	O1-Co1-N1	70.7(8)
Co1-N2	2.101(2)	O1F-Co1-N2	99.4(6)	O3E-Co1-Cl	78.3(6)
Co1-O1	2.376(1)	O3E-Co1-N1	100.3(6)	O1F-Co1-Cl	79.0(4)
Co1-O3E	1.989(3)	O1F-Co1-N1	98.9(5)	N2-Co1-Cl	140.8(6)
Co1-O1F	2.019(1)	N2-Co1-N1	75.1(9)	N1-Co1-Cl	144.1(8)
Co1-Cl	2.700(3)	O3E-Co1-O1	86.9(7)	O1-Co1-Cl	73.5(3)

O3E-Co1-O1F	157.2(7)	O1F-Co1-O1	87.97(3)	N2-Co1-O1	145.7(7)
Co1-N1	2.122(2)	O3E-Co1-N2	97.3(8)	O1-Co1-N1	70.7(8)

Symmetry codes: (A) 1-y, 2+x-y, z; (B) 1-x+y, 1-x, z; (D) -1+y, -x+y, -z;

(E) 1+x-y, 1+x, -z; (F) y-1, -x+y, -z.

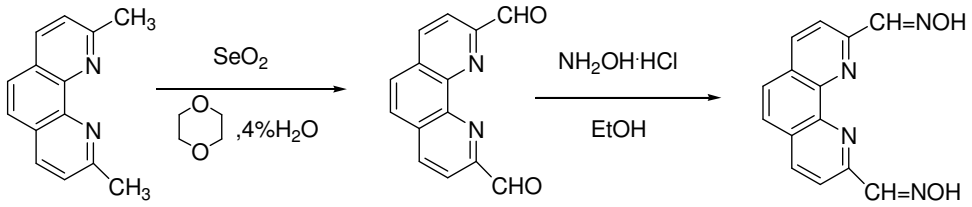
Synthesis of ligand:

1,10-phenanthroline-2,9-dicarbaldehyde[1]

A mixture of neocuproine hemihydrate (2,9-dimethyl-1,10-phenanthroline, 3.0 g, 13.8 mmol) and selenium dioxide (7.5 g) in dioxane containing 4% water (200 ml) was heated under reflux for 2 hours and then filtered through Celite while hot. The dialdehyde (2.8 g, 82%) separated from the cold filtrate as yellow crystals, m.p. 231.5-232.3 °C (231-232 °C[1]).

1,10-phenanthroline-2,9-dicarbaldehyde Dioxime (H_2phenox)[2]

A suspension of dialdehyde (2 g, 8.5 mmol.) in 200 mL of absolute ethanol was stirred at 60 °C for 10 min. $NH_2OH \cdot HCl$ (3.4 g, 44 mmol) was then progressively added within a few minutes, after the addition of pyridine (5 mL, 6.2 mmol), the mixture was stirred at reflux (95 °C) for 2 hours, and then was allowed to cool at room temperature. The precipitate was washed with 100 mL of water to eliminate the excess of $NH_2OH \cdot HCl$, recrystallized from water/DMSO (55:45, v/v) and dried under vacuum (1.6 g, yield 70%), m.p. 265.5-266.3 °C (267 °C [2]).



Scheme S1 Synthesis of ligand H_2phenox.

Elemental analysis and IR data for 1: Elemental analysis (%): calcd (found) for **1** ($Co_6C_{91}H_{62}O_{28}N_{13}Cl$): C, 50.26 (49.01); H, 2.87 (2.35); N, 8.37 (8.85). Selected IR data (KBr pellet, cm^{-1}): 3392(s), 1651(s), 1628(s), 1575(m), 1367(m), 1312(w), 1172(w), 1095(w), 810(w), 714(w).

Elemental analysis and IR data for 2: Elemental analysis (%): calcd (found) for **1** ($Co_6C_{91}H_{62}O_{28}N_{13}F$): C, 49.40 (49.20); H, 3.10 (3.07); N, 8.23 (8.71). Selected IR data (KBr pellet, cm^{-1}): 3417(s), 1652(s), 1575(m), 1375(m), 1313(w), 1174(w), 809(w), 715(w).

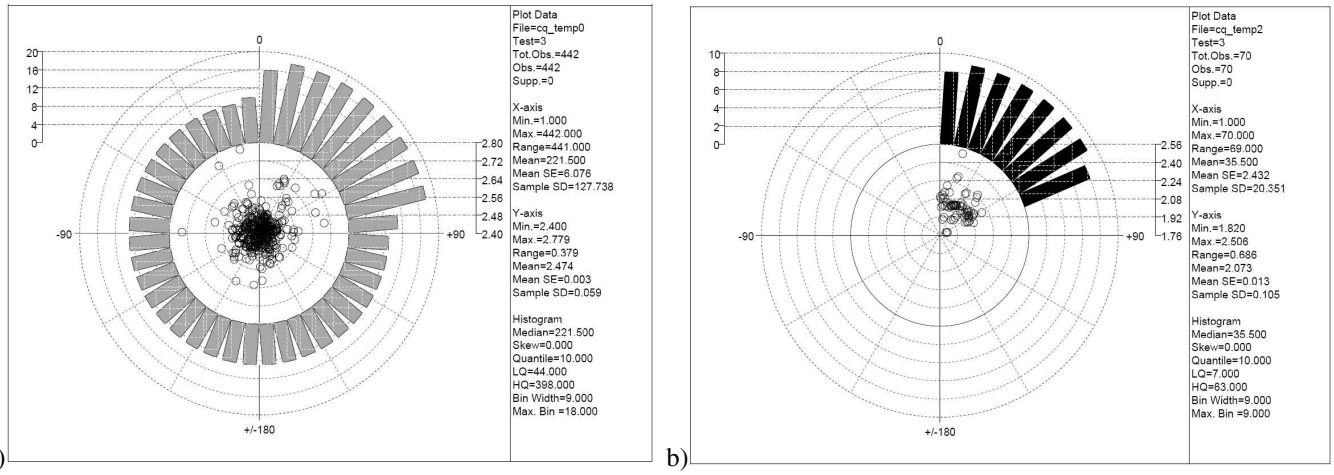


Figure S1 Polar scattergram of the shortest Co–Cl (a) and Co–F (b) bonded distances as retrieved from the CSD. This

scattergram was generated by using VISTA. The scattergrams were obtained from a fragment search from of the CSD.[5]

For compound **3**, 173(2) K, Triclinic $P\bar{1}$, a = 10.680(2) Å, b = 11.343(3) Å, c = 12.629(3) Å, α = 73.756(4)º, β = 77.772(3)º, γ = 85.484(4)º, V = 1435.3(5) Å^3, Z = 2, D_c = 1.565 g cm^{-3}, final R_1 = 0.0729 ($I \geq 2\sigma$), wR_2 = 0.2123 (all 5046 data), S = 1.032. Single crystal X-ray analysis reveals the presence of Co^{III} ion in **3** not only testified by the crystal colour, but also the average distance of Co–N bond is 1.964 Å, which is consistent with those for the Co^{III}-based structure.[3] Most importantly, the oxime group have been oxidized partly to carboxyl group, the C–O distance (1.240 Å) and C–O–C angles (125.4º) are quite in agreement with the general carboxylic values.[4]

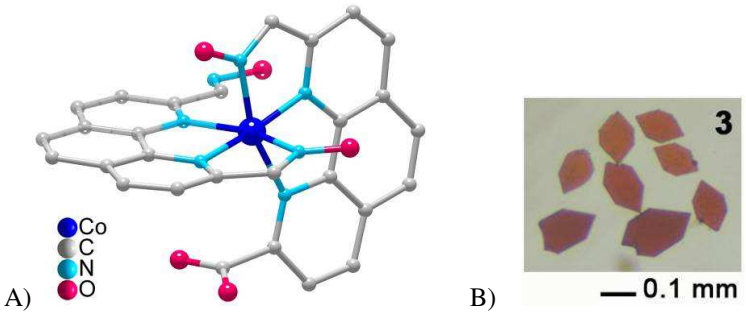
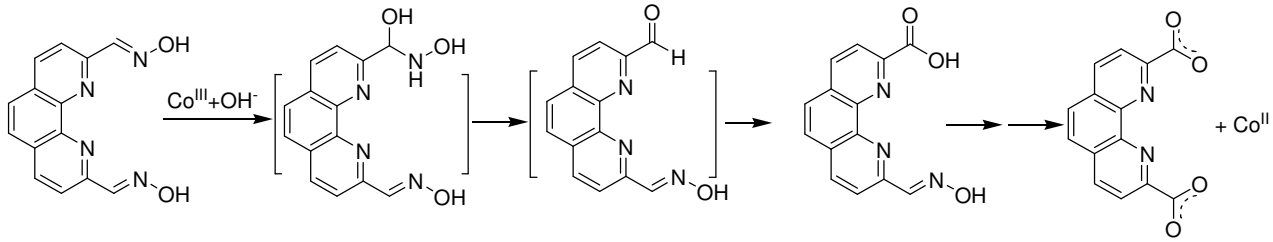


Figure S2 A) The monnuclear structure of **3**, hydrogen atoms and guest molecules have been omitted for clarity; B) photo of the crystals of **3**.



Scheme S2 Proposed course for the transformation from H_2phenox into phendc^{2-}.

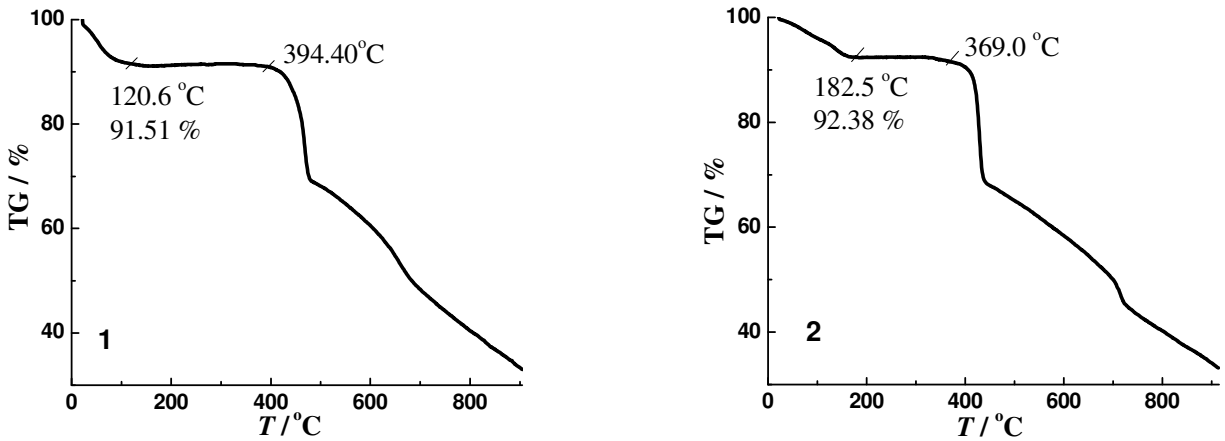


Figure S3. TG curve of **1** and **2** in N_2 atmosphere at a heating rate of 10 °C/min.

The TGA curves show that the weight losses of the samples of **1** at about 120 °C are 8.5%, indicating that the guest molecules and counter ion escape from the crystals (ca. 8.5%), the decomposition of the frameworks began at 394 °C. In the TGA curves of compound **2**, the weight losses at near 182 °C corresponds to the loss of the guest molecules and counter ions (found: 7.6%, ca. 8.6%), complex **2** starts to decompose at 370 °C.

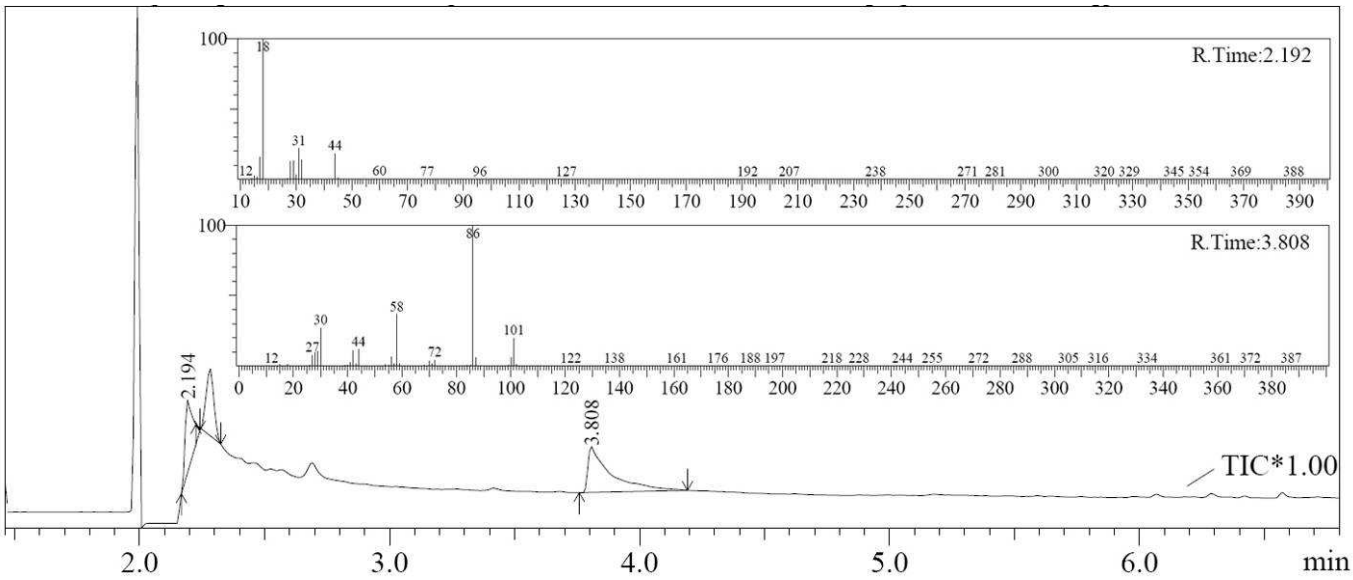


Figure S4. Py-GC/MS measures of **1** at 80 °C.(H_2O m/z: 18, MeOH m/z: 31, NEt_3 m/z:86)

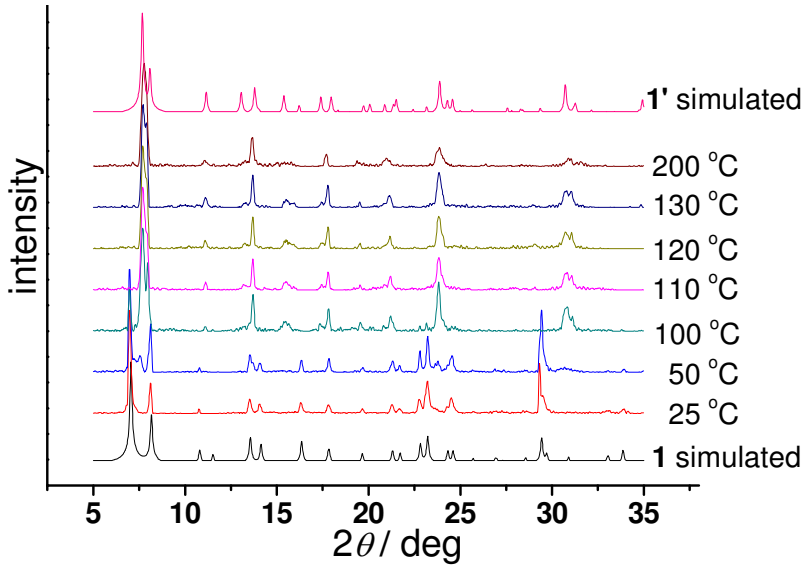


Figure S5a Temperature-dependent X-ray power diffraction for **1**, and the simulated powder X-ray diffraction patterns of **1** and **1′**. The heating rate between the diffraction measurements was 5 °C/min, and the temperature was kept for 10 min for each diffraction measurement.

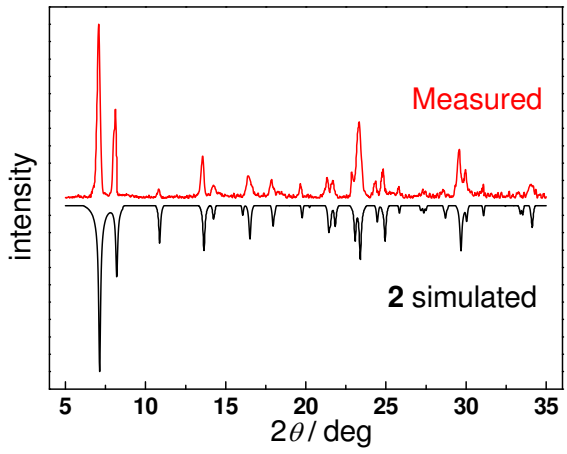


Figure S5b XRD and the simulated patterns of **2**.

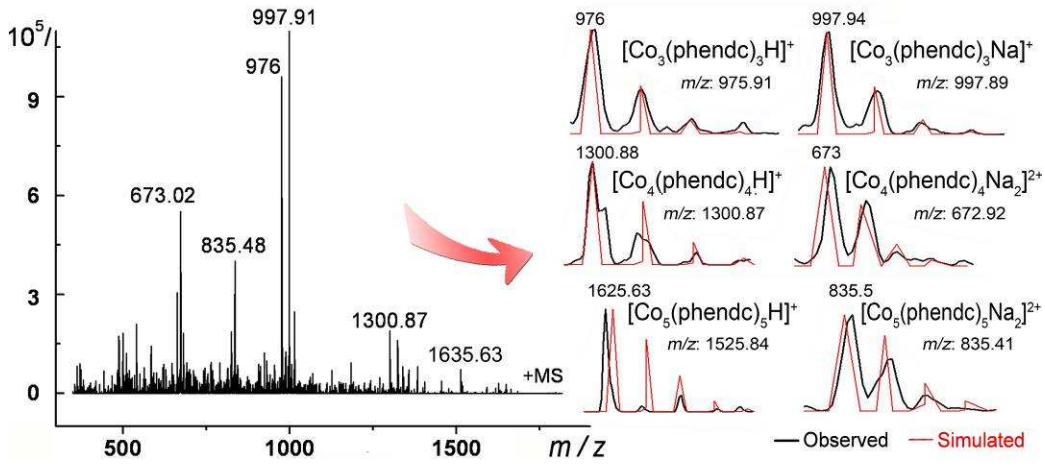


Figure S6 EIS-MS spectra of 2 in acetonitrile.

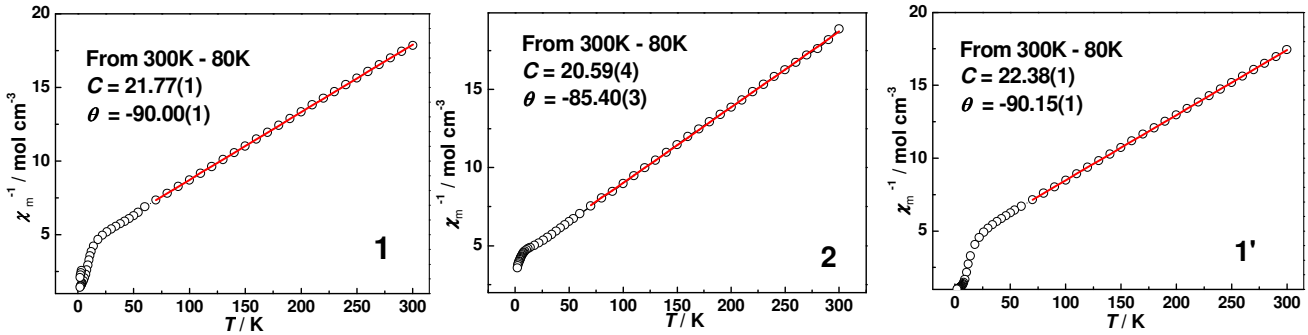


Figure S7. Plots of χ_m^{-1} *vs. T* and the fit of Curie-Weiss law (solid curve) of **1**, **2** and **1′**.

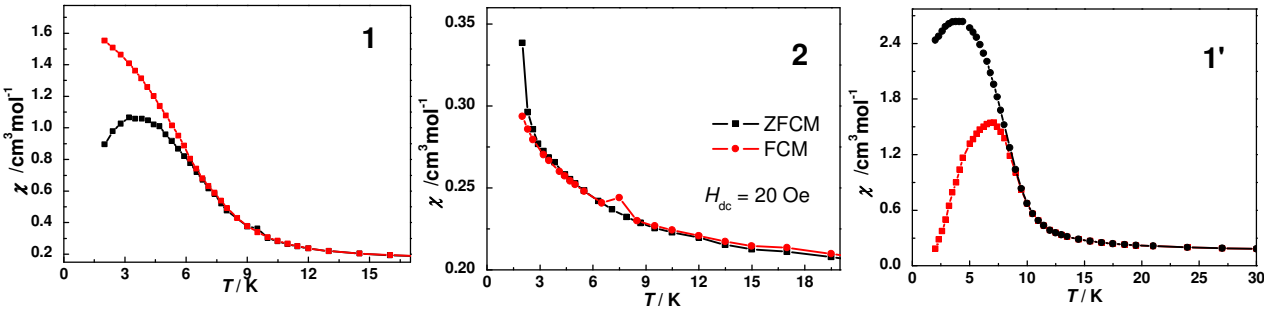


Figure S8. Plots FCM/ZFCM curves of **1**, **2** and **1′**.

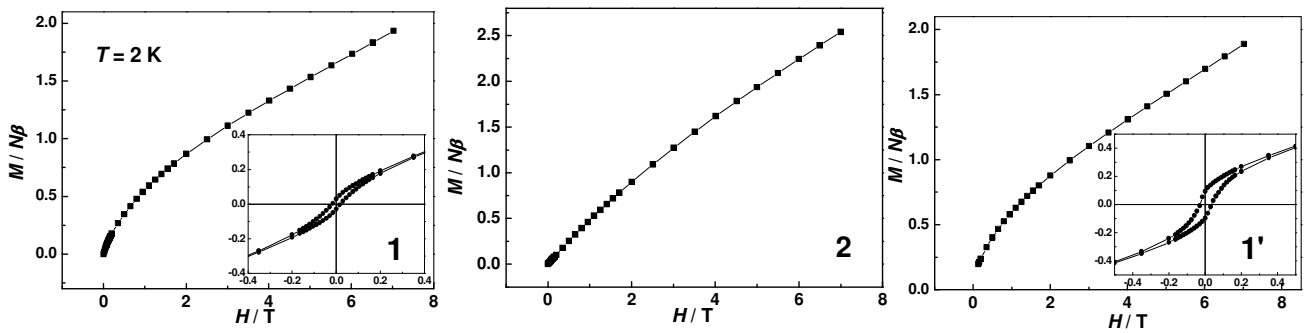


Figure S9. Plots of *M vs. H* and the hysteresis loop (insert) curves of **1**, **2** and **1′** and 2 K.

References

[1] Chandler, C. J.; Deady, L. W.; Reiss. J. A. *J. Heterocyclic Chem*. **1981**, *18*, 599.

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