Unusual assembly of lacunary heteropolymolybdate with cyanometalate fragments

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Experimental details

1. Materials and measurements

All reagents were purchased from commercial sources and used without any further purification. Diffraction data sufficient for unit cell determination for compound **1** was determined on a Bruker Apex CCD diffractometer. The structures were solved using the direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F^2 with WinGX (1.70) program package (L. J. J. Farrugia, *Appl. Crystallogr.* **32**, 837 (1999)). The CCDC data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. CCDC number 914981 for **1**, Elemental analyses (C, H and N) were performed on Flash EA 112 CHN Elemental Analyzer; metal elemental analyses were determined by a Leaman inductively coupled plasma (ICP) spectrometer and SpectrAA-220FS atomic absorption spectrophotometer. Infrared spectra of solid samples were obtained on a BRUKER Vertex 70 FTIR spectrometer in the 400–4000 cm^{-1} region with a KBr pellet. UV electronic spectra were obtained on a Varian Cary 50 Conc UV-vis spectrophotometer. Magnetic susceptibility data were recorded using a Quantum Design SQUID MPMS XL-5 magnetometer.

2. Synthesis

Synthesis of $H_2Na_2(C_4H_{10}ON)_{22}[\{Fe^{III}(CN)_6\}\cdot(Fe^{III}_{0.25}Mn^{II}_{0.75}GeMo_{11}O_{39})_4]\cdot16H_2O$ (1)

$Na_2MoO_4\cdot2H_2O$(0.242 g, 1 mmol) and GeO_2 (0.0209 g, 0.2 mmol) were dissolved in water (15 mL) and stirred until the solution became homogeneous, followed by the addition of morpholine (0.4 mL, 4.59 mmol) and NaCl (4 mL of 2.5 M). The pH value was adjusted to 5.5-5.8 with 6 M HCl and carefully adjusted to 4.9 by addition of 1 M HCl. Then, 5 mL of 0.025 M $K_3[Fe(CN)_6]$ aqueous solution (0.125 mmol) was added, followed by the addition of 5 mL of 0.01 M $MnSO_4$ aqueous solution (0.05 mmol). The resulting orange reaction mixture was then heated to 82 ℃ about 2 h then cooled to room temperature. The mixture was filtered and the dark orange filtrate was kept at room temperature. After 2 days, a brown-yellow by-product formed, which was proved to be $[Mn_2(GeMo_9O_{34})_2]^{16-}$ (identified by infrared spectroscopy, elemental analysis). The by-product microcrystals were removed by filtration and then dark blue block crystals of **1** were obtained after 8 days. (yield: 12% based on Mo) Elemental analysis (%), calcd for $C_{94}H_{254}Fe_2Ge_4Mn_3Mo_{44}N_{28}Na_2O_{194}$: C, 11.60; H, 2.63; N, 4.03; Na, 0.47; Mn, 1.70; Fe, 1.15; Ge, 2.99; Mo, 43.45; Found: C, 11.89; H,2.90 ; N,4.37 ; Na, 0.49; Mn, 1.49; Fe, 1.01.; Ge, 2.80; Mo, 43.12.

Synthesis of $Na_2(C_4H_{10}ON)_{21}[\{Fe^{III}(CN)_6\}\cdot(Fe^{III}GeMo_{11}O_{39})_4]\cdot CH_3CN\cdot11H_2O$ (2)

$Na_2MoO_4\cdot2H_2O$ (0.242 g, 1 mmol) and GeO_2 (0.0209 g, 0.2 mmol) were dissolved in water (15 mL) and stirred until the solution became homogeneous, followed by the addition of morpholine (0.45 mL, 5.16 mmol) and NaCl (0.25 g, 4.28 mmol). The pH value was adjusted to 5.0-5.2 with 6 M HCl and carefully adjusted to 4.5 by addition of 1 M HCl. Then, 5 mL of 0.05 M $K_3[Fe(CN)_6]$ aqueous solution (0.25 mmol) was added, followed by the addition of $FeCl_3\cdot6H_2O$ (0.027 g, 0.1 mmol). The resulting dark green reaction mixture was then heated to 82 ℃ about 2 h then cooled to room temperature. The mixture was filtered and CH_3CN (10 mL) was added to the resulting filtrate. The solution was then finely adjusted to pH 4.4 using dilute hydrochloric acid. The solution was then left to crystallize by slow evaporation. Dark blue block crystals formed after approximately ten days. (yield: 19% based on Mo) Elemental analysis (%), calcd for $C_{92}H_{235}Fe_5Ge_4Mo_{44}N_{28}Na_2O_{184}$: C, 11.54; H, 2.47; N, 4.09; Na, 0.48; Fe, 2.92; Ge, 3.03; Mo, 44.07; Found: C, 11.92; H,2.72 ; N,4.46 ;

Na, 0.62; Fe, 2.77.; Ge, 3.24; Mo, 44.35.

3. Comparative test

Experimental details

(A) Morpholine (0.4 mL, 4.59 mmol) was added to water (20 mL) and the pH adjusted to 4.9 using 6 M HCl and 0.2 M HCl. $K_3[Fe(CN)_6]$ (0.08 g, 0.24mmol) was added to this solution to yield solution A. Then solution A was heated to 80 ^{o}C.

(B) $K_3[Fe(CN)_6]$ (0.08 g, 0.24mmol) was added to water (15 mL, pH = 4.9) to yield solution B. Then solution B was heated to 80 ^{o}C.

Phenomenon

(a) Solution A before being heated

(b) Solution A after being heated at 80 ^{o}C for 10 minutes.

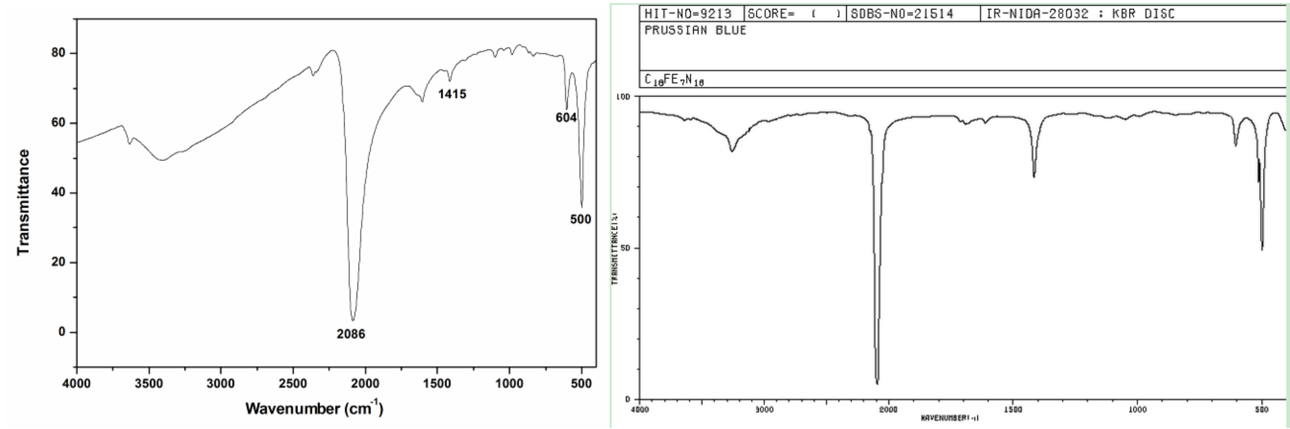
The color of solution A changed from yellow to green, which proves a chemical reaction takes place in the system.

(c) Solution A after being heated at 80 ^oC for 1 hour.

The blue precipitate was collected by filtration. This precipitate is proved to be Prussian blue analogues by IR analyses as below (Fig. S1).

(d) Solution A after being heated at 80 ^oC for 1 hour (left); Solution B after being heated at 80 ^oC for 1 hour (right).

IR of the blue precipitate



(1) (2)

Fig. S1 (1) IR of spectra of the blue precipitate (the band at 2086 cm^{-1} is attributed to *v* (C≡N) stretch.) (2) IR of Prussian blue (from the web of Spectral Database for Organic Compounds SDBS http://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi)

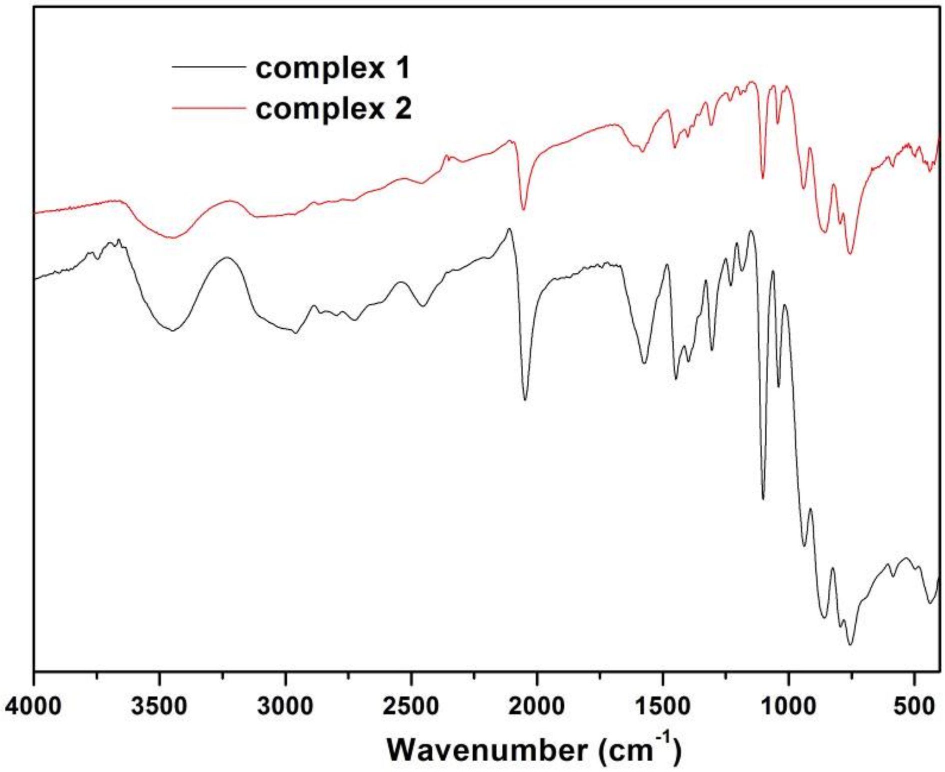


Fig. S2 IR of spectra of **1** and **2**.

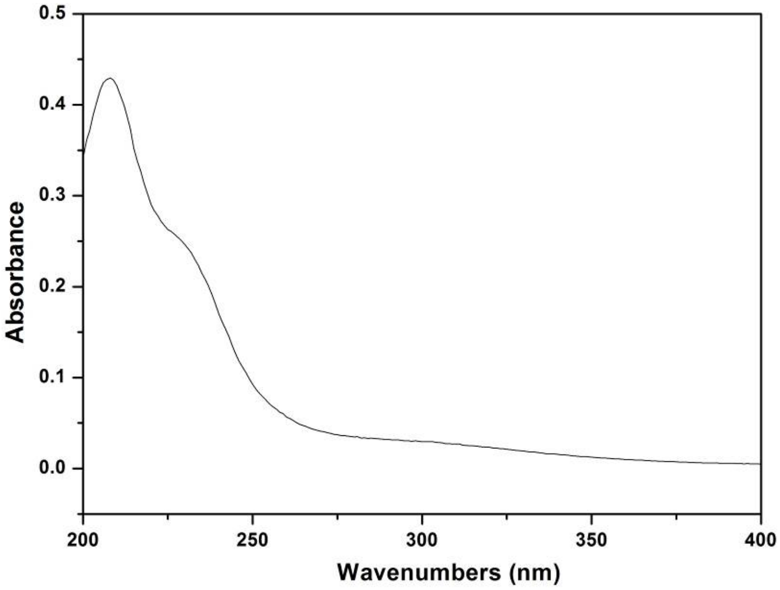


Fig. S3 Electronic absorption spectra of 1 (200-400nm, 2.0×10^{-6} *M* aqueous solution). Two absorption bands at 208 nm and 232 nm characterize the charge transfer transition of $O_t \rightarrow Mo$ and $O_{b,c} \rightarrow Mo$ in complex **1**.

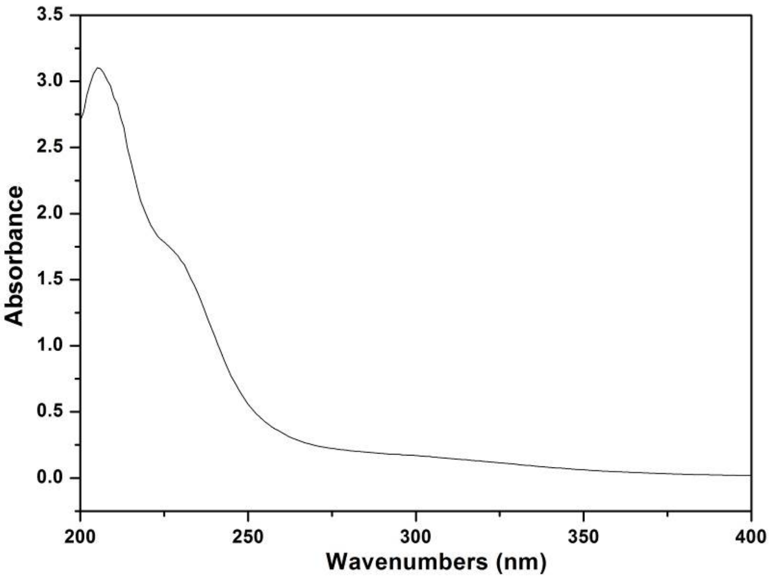


Fig. S4 Electronic absorption spectra of 2 (200-400nm, 2.0×10^{-6} *M* aqueous solution). Two absorption bands at 205 nm and 233 nm characterize the charge transfer transition of $O_t \rightarrow$ Mo and $O_{b,c} \rightarrow$ Mo in complex **2**.

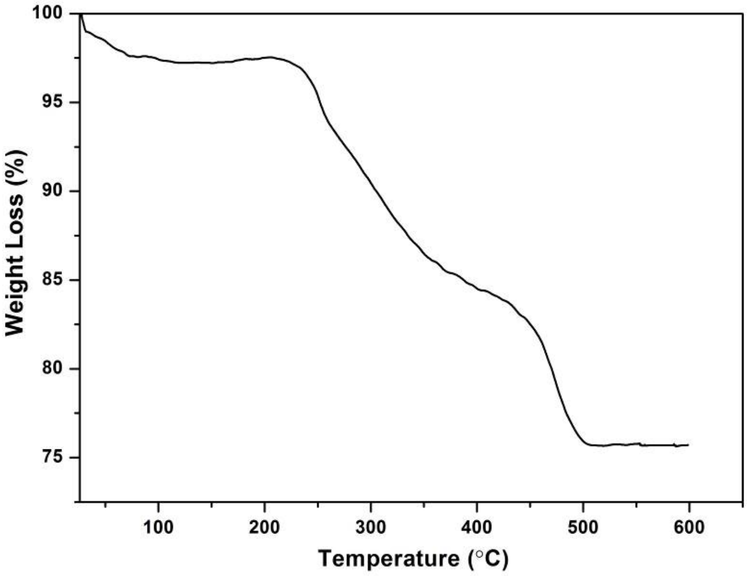


Fig. S5 The TG curve of complex 1. The TG curve of Compound **1** exhibits two steps of weight loss in the range of 30-600 °C. The first weight loss of 2.90% from 30-115 °C corresponds to 16 molecules of water (calc. 2.96%). The second weigh loss is from 217 to 490 °C with a value of 21.6%, which is assigned to the loss of 22 molecules of morpholine ligands and 6 CN^-(calc. 21.5%), accompanied with the decomposotion of the main structure.

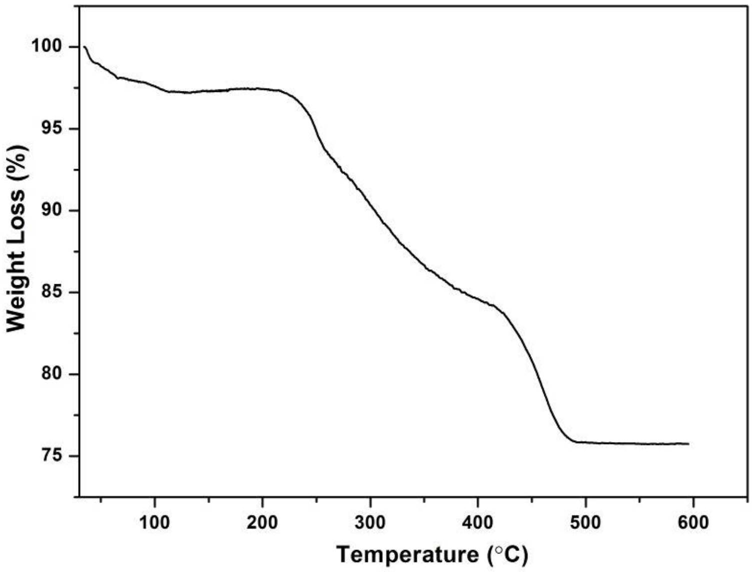


Fig. S6 The TG curve of complex **2**. The TG curve of Compound **2** is similar to that of **1**. The first weight loss of 2.60% from 30-125 ˚C is attributed to the loss of 11 water molecules and 1 acetonitrile molecule. The second weigh loss is from 205 to 470 ˚C with a value of 20.8%, which is assigned to the loss of 21 molecules of morpholine ligands and 6 CN$^-$(calc. 20.9%), accompanied with the decomposotion of the main structure.

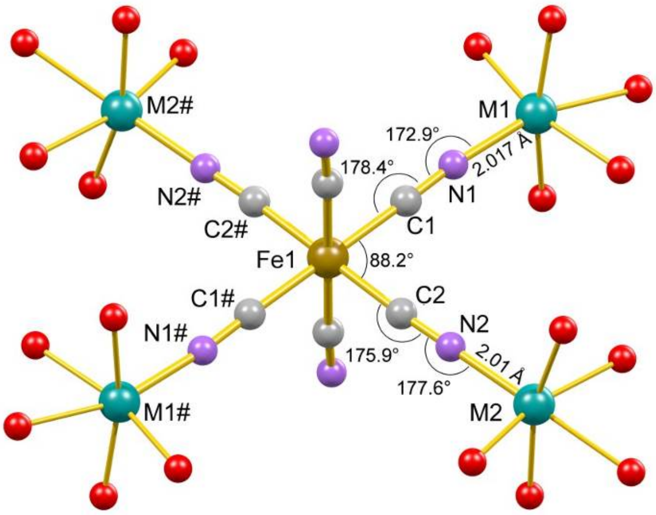


Fig. S7 ball-and-stick representation of the [$Fe^{III}_2Mn^{II}_2Fe(CN)_6$] unit in **1** (O-red).

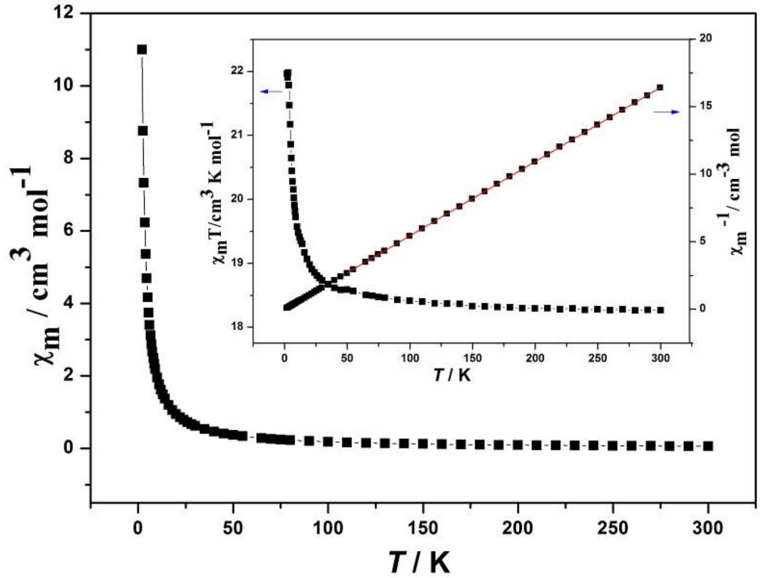


Fig. S8 Plot of χ_m vs T for **1**. Plots of $\chi_\mathrm{m}T$ and χ_m^{-1} versus T for **1** are shown in the inset. Good fit is obtained and shown by red solid line.

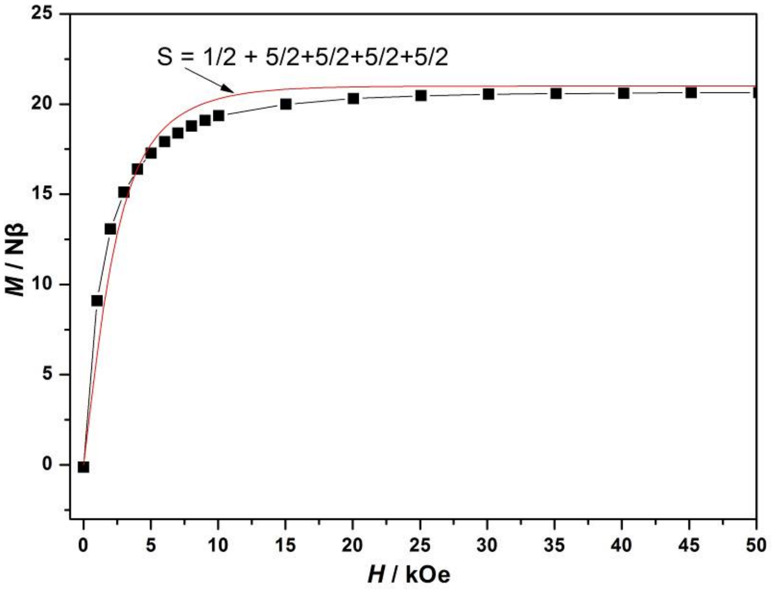


Fig. S9 Field dependence of magnetization of **1** at 0.5 K. The solid line represents the Brillouin function that corresponds to non-interacting $S = 1\times S_{Fe} + 3\times S_{Mn} + 1\times S_{Fe}$ with $g = 2.0$.

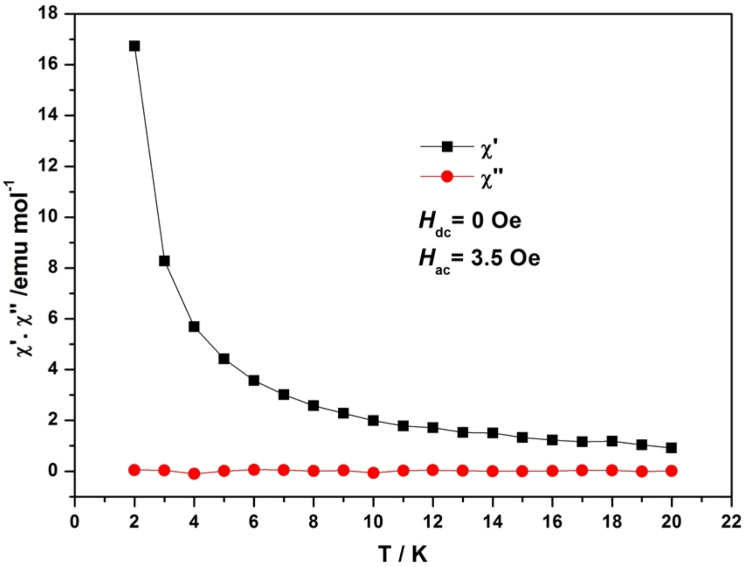


Fig. S10 Temperature dependence of the real (top) and imaginary (bottom) components of the ac susceptibility in zero applied static field with an oscillating field of 3.5 Oe at a frequency of 100 Hz for compound **1**.

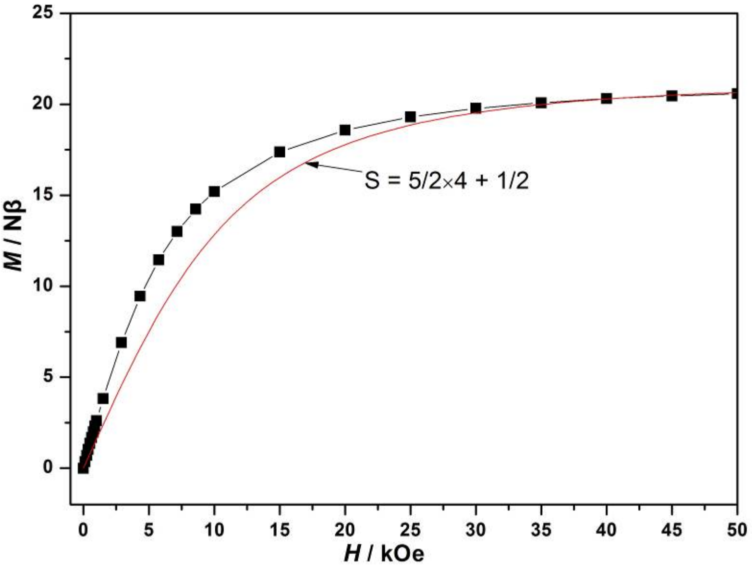


Fig. S11 Field dependence of magnetization of **2** at 2 K. The solid line represents the Brillouin function that corresponds to non-interacting S = 4×S_{Fe} + 1×S_{Fe} with g = 2.0.

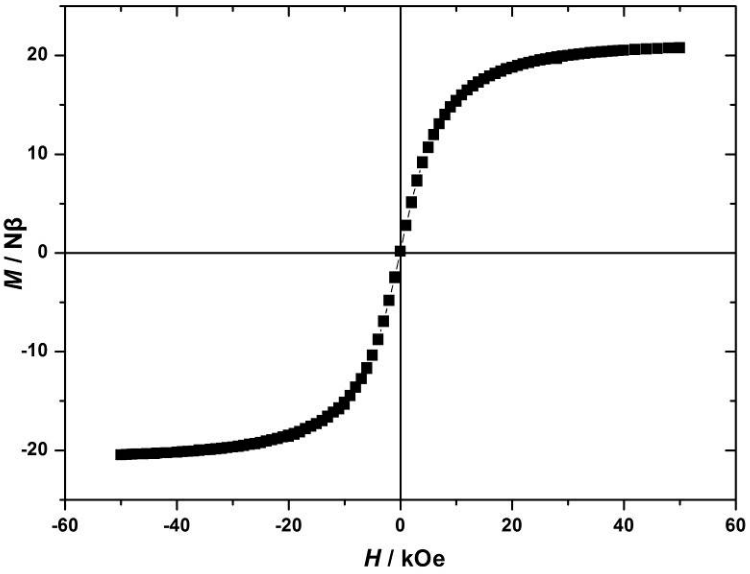


Fig. S12 Hysteresis loop at 2 K for compound **2**.

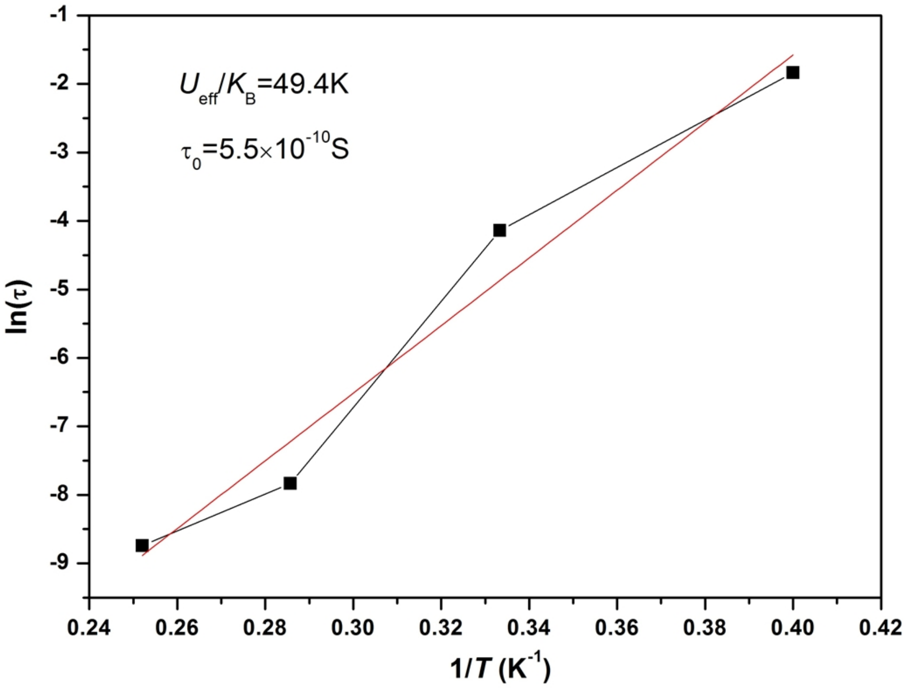


Fig. S13 Plot of the natural logarithm of the relaxation time τ against the inverse of the temperature T for **2**. The solid line is a fit of the Arrhenius law to indicated parameters of **2**.

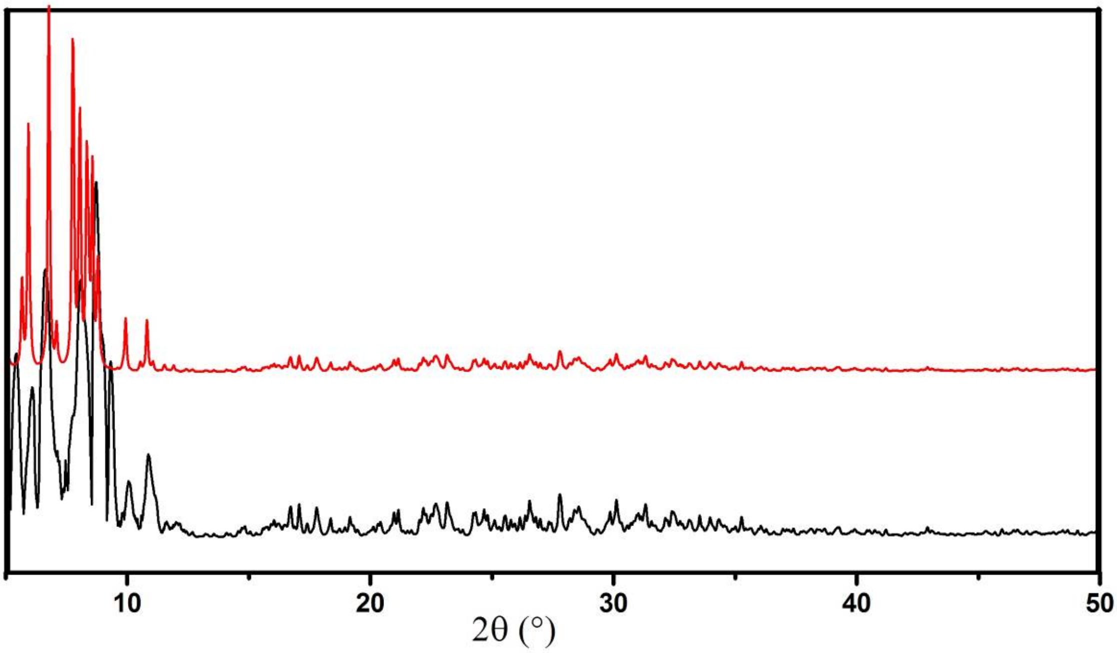


Fig. S14 Powder XRD pattern of **1** (black line) and simulated powder XRD pattern from data collected from a single crystal of **1** (red line).

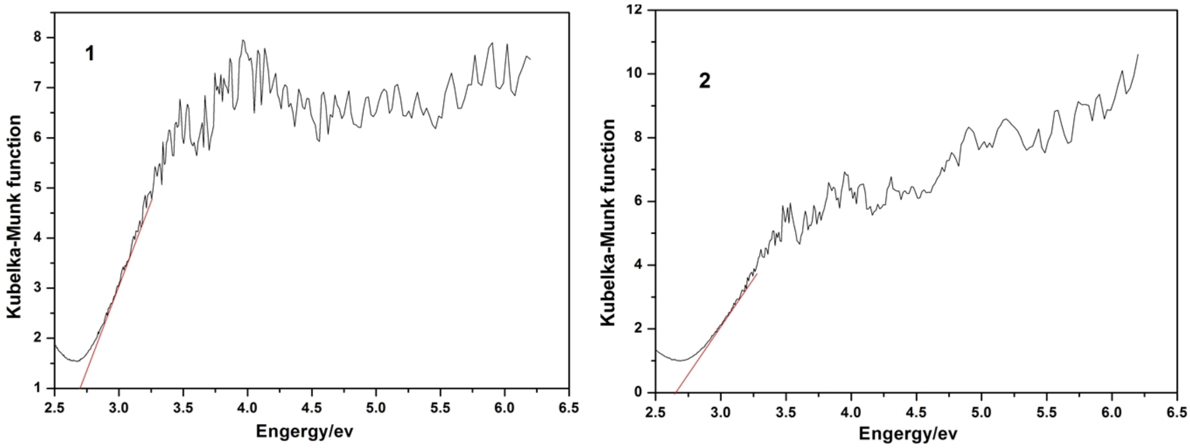


Fig. S15 Diffuse reflectance UV-vis spectra of *K*-*M* function versus *E* (eV) of compounds **1** and **2**. The E_g values assessed from the steep absorption edge are 2.65 and 2.68 eV for compound **1** and **2**, respectively, which are smaller than that of $H_4GeMo_{12}O_{40}$ (3.11 eV).

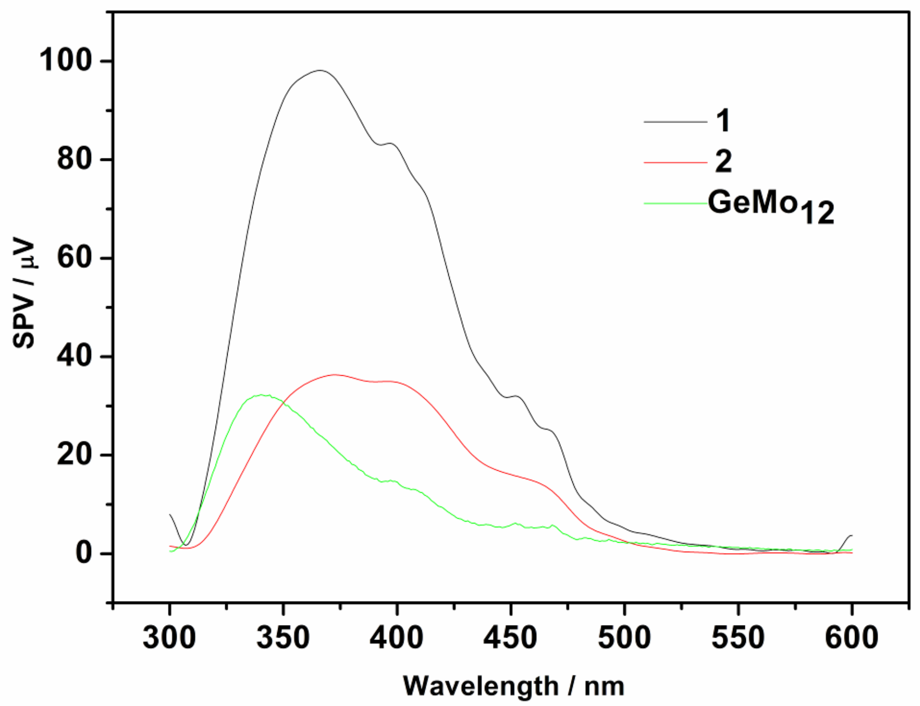


Fig. S16 Surface photovoltage spectra of compounds **1**, **2** and $H_4GeMo_{12}O_{40}$ ($GeMo_{12}$) under a positive electric field of 1V. The pronounced surface photovoltage (SPV) response bands in the range of 310-500 nm correspond to the excitation transition. Blue shifts occurred in the SPV responses of **1** and **2** compared with that of $GeMo_{12}$, due to the incorporation of the metal-cyano fragments.

Table S1 Crystal Data and Structure Refinement for **1**.

Empirical formula	$C_{94}H_{254}Fe_2Ge_4Mn_3Mo_{44}N_{28}Na_2O_{194}$
Formula weight	9715.47
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 16.980(2) Å, α= 103.893(2)°
	b = 22.097(3) Å, β= 108.851(2)°
	c = 23.703(3) Å, γ= 104.898(2)°
Volume	7608.7(16) Å^3
Z	1
Calculated density	2.120 g/cm^3
Absorption coefficient	2.417 mm^{-1}
F(000)	4691
Crystal size	0.20 x 0.18 x 0.17 mm^3
Theta range for data collection	1.31 to 23.49°
Limiting indices	-18<=h<=18, -22<=k<=24, -26<=l<=25
Reflections collected / unique	33877 / 22203 [R(int) = 0.0487]
Completeness to theta = 23.49°	98.8 %
Max. and min. transmission	0.660 and 0.623
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	22203 / 109 / 1215
Goodness-of-fit on F^2	0.997
Final R indices [I>2sigma(I)]	R_1 = 0.0609, wR_2 = 0.1399
R indices (all data)	R_1 = 0.1303, wR_2 = 0.1527
Largest diff. peak and hole	0.957 and -0.635 e.A^3