

Supporting Information for

Divalent Metal Ions Modulated Strong Frustrated M(II)-Fe(III)₃O (M= Fe, Mn, Mg) Chains with Metamagnetism Only in Mixed Valence Iron Complex

Qi-Long Wu,^a Song-De Han,^b Qing-Lun Wang,^c Jiong-Peng Zhao,^{*a} Feng Ma,^a Xue Jiang,^b Fu-Chen Liu,^{*a} and Xian-He Bu^{*b}

^a School of Chemistry and Chemical Engineering, Tianjin University of Technology, TKL of Organic Solar Cells and Photochemical Conversion, Tianjin 300384, P.R. China.

^b TKL of Metal- and Molecule-Based Material Chemistry, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, P.R. China.

^c Department of Chemistry, Nankai University, Tianjin 300071, P.R. China.

* Corresponding author. Fax: (+86) 22-23502458. E-mail: horryzhao@yahoo.com, fuchenliutj@yahoo.com and buxh@nankai.edu.cn

Experimental Section

Materials and methods. All chemicals were reagent grade and used as purchased without further purification. The XRPD spectra were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectrum was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the internet at <http://www.iucr.org>. Elemental analyses of C, H and N were performed on a Perkin-Elmer 240C analyzer. UV-vis spectra were recorded on a VarianCary5000spectrophotometer. Magnetic susceptibility was measured by a Quantum Design MPMS superconducting quantum interference device (SQUID). Diamagnetic corrections were estimated by using Pascal constants and background corrections by experimental measurement on sample holders.

X-ray Crystallography. The single-crystal X-ray diffraction data of **1**, **2** and **3** were collected on a Rigaku SCX-mini diffractometer at 293(2) K. The program *CrystalClear*^{S1} was used for the integration of the diffraction profiles. The structure was solved by direct method using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied by using the SADABS program).^{S2} The non-hydrogen atoms were

located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . All hydrogen atoms were generated theoretically at the specific atoms and refined isotropically with fixed thermal factors. The selected bond lengths and angles are given in Tables S1.

References

- S1. G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
 S2. CrystalClear and CrystalStructure; Rigaku/MSK: The Woodlands, TX, 2005.

Table S1. Selected bond lengths [Å] for **1 - 3**.

1		2		3	
Fe1—O3 ⁱⁱ	2.123 (6)	Fe1—O1	1.947 (11)	Fe1—O1	2.060 (2)
Fe1—O3	2.123 (6)	Fe1—O13	2.017 (14)	Fe1—O12	2.060 (2)
Fe1—O1	2.128 (6)	Fe1—O20	2.019 (12)	Fe1—O14	2.060 (2)
Fe1—O1 ⁱⁱ	2.128 (6)	Fe1—O8	2.019 (14)	Fe1—O2	2.060 (2)
Fe1—O1W	2.160 (6)	Fe1—O7	2.032 (14)	Fe1—O11	2.060 (2)
Fe1—O1W ⁱⁱ	2.160 (6)	Fe1—O10	2.052 (13)	Fe1—O4	2.060 (2)
Fe2—O19	1.905 (6)	Fe2—O1	1.941 (10)	Fe2—O1	1.917 (2)
Fe2—O11	2.025 (7)	Fe2—O11	2.022 (13)	Fe2—O5	2.004 (3)
Fe2—O2 ⁱⁱⁱ	2.029 (6)	Fe2—O12	2.037 (13)	Fe2—O3	2.020 (3)
Fe2—O9	2.034 (7)	Fe2—O2	2.045 (13)	Fe2—O6	2.027 (3)
Fe2—O7	2.053 (6)	Fe2—O5	2.047 (13)	Fe2—O16	2.028 (2)
Fe2—O6	2.064 (7)	Fe2—O17	2.052 (12)	Fe2—O8	2.041 (3)
Fe3—O19	1.938 (6)	Fe3—O1	1.886 (11)	Fe3—O1	1.903 (2)
Fe3—O17	2.016 (6)	Fe3—O9	2.013 (12)	Fe3—O10	2.020 (3)
Fe3—O10	2.018 (7)	Fe3—O6	2.034 (13)	Fe3—O19 ⁱ	2.023 (3)
Fe3—O13	2.030 (7)	Fe3—O14	2.040 (12)	Fe3—O13	2.025 (3)
Fe3—O16	2.030 (6)	Fe3—O3	2.043 (13)	Fe3—O7	2.038 (2)
Fe3—O12	2.034 (7)	Fe3—O4	2.056 (12)	Fe3—O9	2.054 (2)
Fe4—O19	1.946 (6)	Mn1—O16 ⁱⁱ	2.193 (12)	Mg1—O17 ⁱⁱ	2.074 (2)
Fe4—O14	2.016 (7)	Mn1—O16 ⁱⁱⁱ	2.193 (12)	Mg1—O17	2.074 (2)
Fe4—O15	2.033 (6)	Mn1—O15	2.208 (12)	Mg1—O18 ⁱⁱ	2.084 (2)
Fe4—O8	2.034 (6)	Mn1—O15 ^{iv}	2.208 (12)	Mg1—O18	2.084 (2)
Fe4—O4	2.048 (7)	Mn1—O1W	2.222 (12)	Mg1—O1W	2.098 (3)
Fe4—O5	2.062 (6)	Mn1—O1W ^{iv}	2.222 (12)	Mg1—O1W ⁱⁱ	2.098 (3)
Fe2—O19—Fe3	120.3 (3)	Fe3—O1—Fe2	121.3 (6)	Fe3—O1—Fe2	120.79 (11)
Fe2—O19—Fe4	120.4 (3)	Fe3—O1—Fe1	120.5 (5)	Fe3—O1—Fe1	119.54 (12)
Fe3—O19—Fe4	119.2 (3)	Fe2—O1—Fe1	118.1 (5)	Fe2—O1—Fe1	119.61 (11)

ⁱⁱ $-x+1, -y+1, -z$; ⁱⁱⁱ $x-1, y-1, z$.
ⁱⁱ $-x+1, -y, -z$; ⁱⁱⁱ $x-1, y-1, z$;
^{iv} $-x, -y-1, -z$.

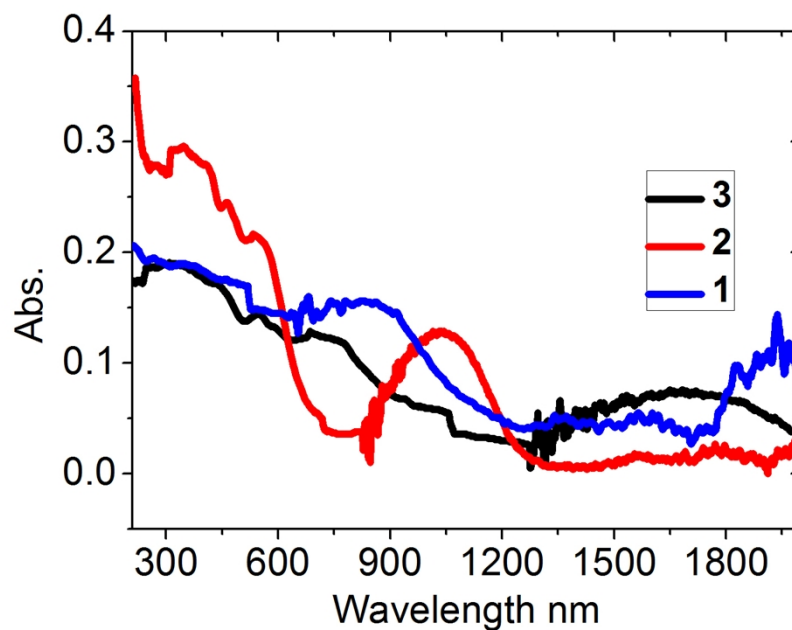


Fig. S1 The UV spectrum for 1-3.

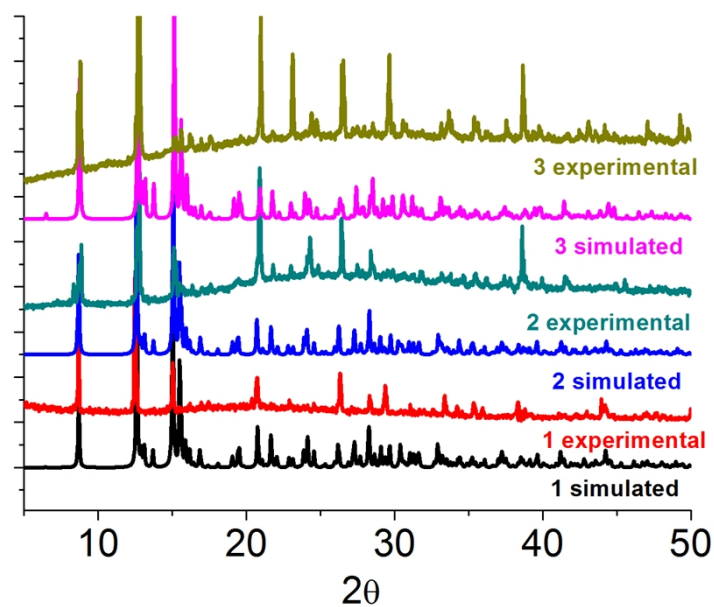


Fig. S2 Powder X-ray diffraction pattern of 1-3.

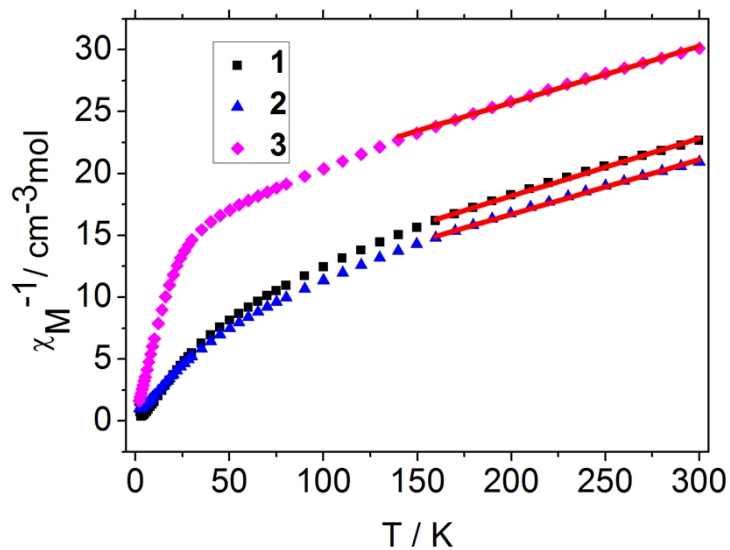


Fig. S3 χ_M^{-1} vs. T plots of **1**, **2** and **3**. The red lines are the fitting by the Curie–Weiss law.

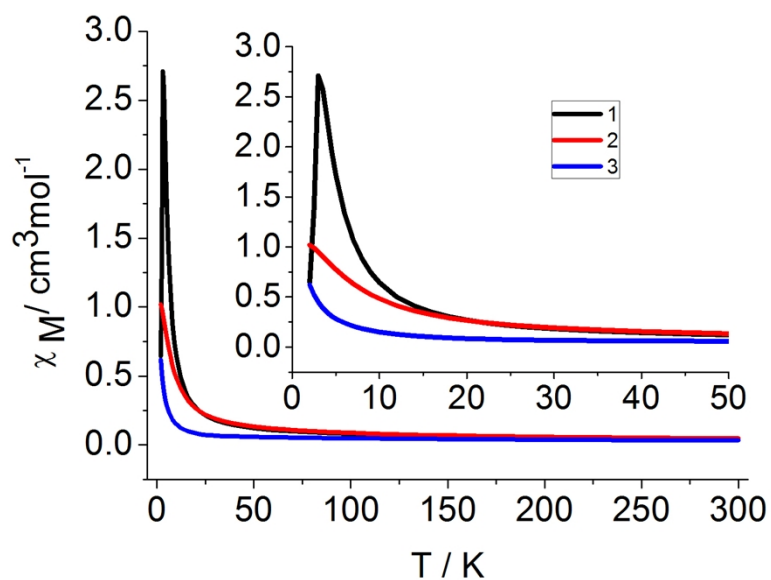


Fig. S4 The χ_M vs. T plots of **1**, **2** and **3**.

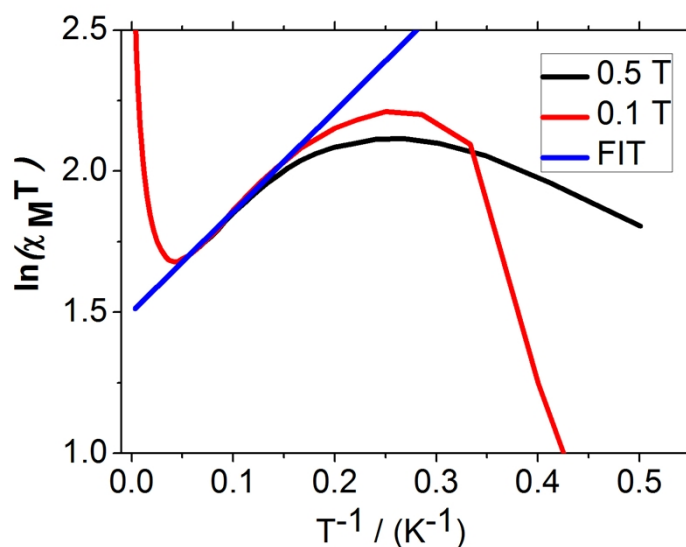


Fig. S5 Logarithm of $\chi_M T$ vs. $1/T$ plot of **1**. The blue line is the result of fitting by $\chi_M T = C_{eff} \exp(\Delta/k_B T)$ between 20 K and 8 K with the energy gap of $\Delta/k_B = 3.38$ K and $C_{eff} = 4.51$ cm³ mol⁻¹ K.

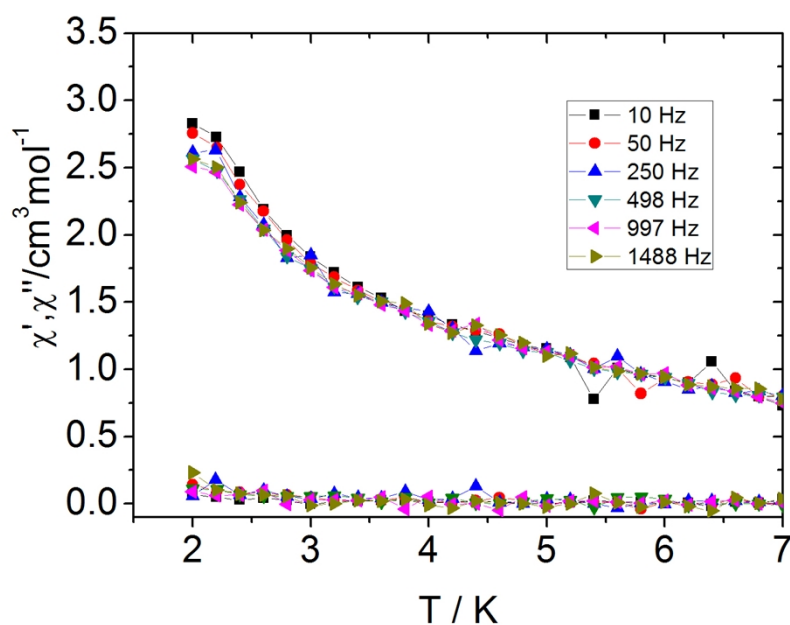


Fig. S6 AC plot for **1** between 2 K and 7 K at different frequencies under a DC field of 0.4 T.