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# Supporting Information

## Coligand phenylacetic acid effect on structure and magnetic property of azido-bridged copper(II)-chains compounds

Lan Yang,[a] Sheng Zhang,[a] Xiangyu Liu,[a,b] Qi Yang,[a] Qing Wei,[a] Gang Xie,[a] Sanping Chen*[a]

[a] *Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an, 710069, China*

[b] *School of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China*

**Corresponding author**

**Dr. Sanping Chen**

**Tel.: +8602988302604**

**Fax: +8602988302604**

**E-mail:** sanpingchen@126.com; sanpingchen312@gmail.com

**Table S1.** Selected bond lengths [Å] and angles [°] for compound **1**.

| | | | |
|---|---|---|---|
| O(2)-Cu(1)#1 | 1.942(2) | O(2)#2-Cu(1)-N(1)#2 | 93.29(10) |
| Cu(1)-O(1) | 1.925(2) | N(1)-Cu(1)-N(1)#2 | 175.42(2) |
| Cu(1)-O(2)#2 | 1.942(2) | O(1)-Cu(1)-O(5) | 91.56(10) |
| Cu(1)-O(5) | 2.419(3) | C(8)-O(2)-Cu(1)#1 | 129.3(2) |
| Cu(1)-N(1) | 2.003(2) | O(2)#2-Cu(1)-O(5) | 93.05(10) |
| Cu(1)-N(1)#2 | 2.019(2) | N(1)-Cu(1)-O(5) | 85.26(11) |
| N(1)-Cu(1)#1 | 2.019(2) | N(1)#2-Cu(1)-O(5) | 96.75(11) |
| N(1)-N(2) | 1.214(4) | C(8)-O(1)-Cu(1) | 134.5(2) |
| N(2)-N(3) | 1.133(4) | N(2)-N(1)-Cu(1) | 120.7(2) |
| O(1)-Cu(1)-O(2)#2 | 175.30(10) | N(2)-N(1)-Cu(1)#1 | 116.2(2) |
| O(1)-Cu(1)-O(2)#2 | 88.77(10) | Cu(1)-N(1)-Cu(1)#1 | 110.40(12) |
| O(1)-Cu(1)-N(1) | 90.70(10) | N(3)-N(2)-N(1) | 177.70(4) |
| O(2)#2-Cu(1)-N(1) | 87.07(10) | | |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,-z+1/2 #2 -x+1/2,y-1/2,-z+1/2

**Table S2.** Selected bond lengths [Å] and angles [°] for compound **2**.

| | | | |
|---|---|---|---|
| Cu(1)-O(1)#1 | 1.917(10) | O(1)-Cu(1)-N(1)#1 | 88.5(5) |
| Cu(1)-O(1) | 1.917(10) | N(1)-Cu(1)-N(1)#1 | 180.0(1) |
| Cu(1)-N(1) | 1.917(11) | O(2)#2-Cu(2)-O(2) | 180.0(2) |
| Cu(1)-N(1)#1 | 1.917(11) | O(2)#2-Cu(2)-N(1) | 88.7(4) |
| Cu(2)-O(2)#2 | 1.934(10) | O(2)-Cu(2)-N(1) | 91.3(4) |
| Cu(2)-O(2) | 1.934(10) | O(2)#2-Cu(2)-N(1)#2 | 91.3(4) |
| Cu(2)-N(1) | 1.993(11) | O(2)-Cu(2)-N(1)#2 | 88.7(4) |
| Cu(2)-N(1)#2 | 1.993(11) | N(1)-Cu(2)-N(1)#2 | 180.0(1) |
| N(1)-N(2) | 1.189(16) | C(1)-O(1)-Cu(1) | 134.6(10) |
| N(2)-N(3) | 1.160(18) | C(1)-O(2)-Cu(2) | 135.3(9) |
| O(1)#1-Cu(1)-O(1) | 180.0(2) | N(2)-N(1)-Cu(1) | 121.3(10) |
| O(1)#1-Cu(1)-N(1) | 88.5(5) | N(2)-N(1)-Cu(2) | 117.7(9) |
| O(1)-Cu(1)-N(1) | 91.5(5) | Cu(1)-N(1)-Cu(2) | 120.4(6) |
| O(1)#1-Cu(1)-N(1)#1 | 91.5(5) | N(3)-N(2)-N(1) | 178.0(2) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+1 #2 -x,-y+2,-z+1

**Table S3.** Selected bond lengths [Å] and angles [°] for compound **3**.

| | | | |
|---|---|---|---|
| Cu(1)-O(12)#1 | 1.926(4) | O(1)-Cu(1)-N(3) | 94.0(2) |
| Cu(1)-O(1) | 1.960(4) | O(12)#1-Cu(1)-N(3)#1 | 93.0(2) |
| Cu(1)-N(3) | 1.973(5) | O(1)-Cu(1)-N(3)#1 | 90.1(2) |
| Cu(1)-N(3)#1 | 1.979(5) | N(3)-Cu(1)-N(3)#1 | 152.29(9) |
| N(3)-Cu(1)#2 | 1.979(5) | N(2)-N(1)-N(3) | 178.7(7) |
| O(12)-Cu(1)#2 | 1.926(4) | N(1)-N(3)-Cu(1) | 118.0(4) |
| N(1)-N(2) | 1.125(7) | N(1)-N(3)-Cu(1)#2 | 118.7(4) |
| N(1)-N(3) | 1.225(8) | Cu(1)-N(3)-Cu(1)#2 | 122.4(3) |

| | | | |
|---|---|---|---|
| O(12)#1-Cu(1)-O(1) | 164.77(19) | C(9)-O(1)-Cu(1) | 129.6(4) |
| O(12)#1-Cu(1)-N(3) | 90.1(2) | C(9)-O(12)-Cu(1)#2 | 127.6(4) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y-1/2,-z+3/2 #2 -x+2,y+1/2,-z+3/2

**Table S4**. Structural and magnetic parameters for Cu(II)-azido mixed-bridged compounds.

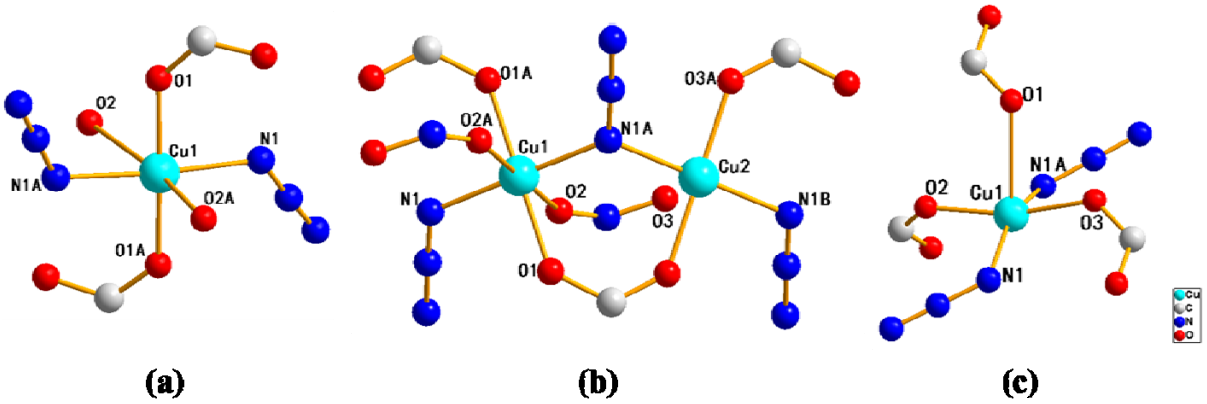
| Year | Unit | Formula | Dimension | Cu-N-Cu(°) | Cu⋯Cu(Å) (intrachain) | $\chi_M T$ (300 K) ($cm^3\ mol^{-1}\ K$) | $J^a$($cm^{-1}$) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1997 | 2Cu | $[Cu_2(N_3)_2(NO_3)_2(L^1)_2]_n$ | 1D | 119.5 | 3.44 | 0.62 | 26 | 17 |
| | 1Cu | $\{[Cu(Hpht)(N_3)]H_2O\}_n$ | 1D | 111.9 | 3.28 | 0.60 | 75 | 16 |
| 2006 | 1Cu | $[Cu(INO)(N_3)(H_2O)_{0.5}]_n$ | 3D | 106.6 | 3.22 | 0.64 | 80 | 10*c* |
| | 1Cu | $[Cu(NNO)(N_3)(H_2O)_{0.5}]_n$ | 2D | 124.3 | 3.52 | 0.57 | 48 | 10*c* |
| | 1.5Cu | $[Cu_{1.5}(N_3)_2(isonic)]_n$ | 3D | 106.7 | 3.20 | 1.40 | 80 | 21*a* |
| 2007 | 3Cu | $[Cu_3((R)\text{-phea})_2(N_3)_6]_n$ | 2D | 101.8 | 3.04 | 1.27 | 15.27 | 21*b* |
| | 3Cu | $[Cu_3((S)\text{-phea})_2(N_3)_6]_n$ | | | | | | |
| | 1Cu | $[Cu(N_3)(nic)]_n$ | 3D | 113.6 | 3.35 | 0.54 | 39.1 | 21*c* |
| | 1.5Cu | $[Cu_{1.5}(hnta)(N_3)_2(H_2O)]_n$ | 1D | 103.2 | 3.12 | 0.80 | 89 | 15*a* |
| | 3Cu | $[Cu_3(hnta)_4(N_3)_2(H_2O)_3]_n$ | 0D | 116.2 | 3.39 | 1.60 | 69.7 | 15*a* |
| 2008 | 1Cu | $[Cu(N_3)(tp)(CH_3OH)]_n$ | 2D | 105.5 | 3.19 | 0.54 | 63 | 21*d* |
| 2009 | 2Cu | $[Cu_2(4\text{-pya})_2(N_3)_2(DMF)]_n$ | 2D | 102.1 | - | 0.98 | 145 | 10*b* |
| | 1Cu | $[Cu(benzoate)(N_3)]_n$ | 1D | 126.8 | 3.54 | 0.56 | 33.90 | 11*a* |
| | 1Cu | $[Cu(L^2)(N_3)]_n$ | 2D | 108.2 | 3.23 | 0.59 | 93.10 | 11*a* |
| | 1Cu | $[Cu(1\text{-naphthoate})(N_3)]_n$ | 2D | 116.8 | 3.41 | 0.61 | 65.63 | 11*a* |
| | 1Cu | $[Cu(N_3)(p\text{-CPA})]_n$ | 2D | 107.0 | 3.18 | 0.52 | 68.82 | 22*a* |
| 2010 | 1Cu | $[Cu(2\text{-Clnic})(N_3)(CH_3OH)]_n$ | 1D | 110.3 | 3.29 | - | 81.22 | 22*b* |
| | 3Cu | $[Cu_3(pyz)_2(N_3)_6]_n$ | 2D | 100.5 | 3.09 | 1.39 | 118.8 | 22*c* |
| 2011 | 1Cu | $[Cu(mptz)(N_3)_2]_n$ | 1D | 103.3 | 3.15 | 0.48 | 65.4 | 22*d* |
| | 1Cu | $[Cu(4,3\text{-pybz})(N_3)]_n$ | 2D | 109.4 | 3.25 | 0.52 | 63.9 | 11*c* |
| | 2Cu | $[Cu_2(4,4\text{-pybz})_3(N_3)]_n \cdot 3nH_2O$ | 3D | 101.1 | 3.08 | 0.91 | 93.6 | 11*c* |
| 2012 | 4Cu | $[Cu_4(N_3)_8(Me\text{-hmpz})_2]_n$ | 1D | 101.0 | 3.11 | 1.66 | $J_1$=40.57 $J_2$=28.47 | 22*e* |
| | 4Cu | $[Cu_4(N_3)_8(men)_2]_n$ | 1D | 102.2 | 3.40 | 1.75 | $J_1$=57.97 $J_2$=-14.03 | 22*e* |
| | 5Cu | $[Cu_5(N_3)_{10}(N,N\text{-dmen})_2]_n$ | 2D | 101.6 | 3.40 | 1.68 | $J_1$=-494.99 $J_2$=88.60 | 22*e* |
| | 5Cu | $[Cu_5(N_3)_{10}(N,N'\text{-dmen})_5]_n$ | 1D | 102.2 | 3.50 | 1.67 | - | 22*e* |
| 2013 | 4Cu | $[Cu_4(N_3)_8(L^3)_2]_n$ | 1D | 102.9 137.1 | 3.12 4.13 | 1.65 | $J_1$=-0.70 $J_2$=64.9 | 22*f* |
| | 4Cu | $[Cu_4(N_3)_6(L^4)_2(H_2O)_2]$ | 2D | 93.4 102.1 108.9 | 3.10 3.22 | 1.60 | $J_1$=-81.0 $J_2$=112.4 | 22*f* |
| | 4Cu | $[Cu_4(N_3)_6(L^5)_2]_n$ | 1D | 91.8 102.2 | 3.18 3.09 | 1.59 | $J_1$=-77.9 $J_2$=129.9 | 22*f* |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 107.3 | 3.18 | | | |
| Our work | 1Cu | $[Cu(o\text{-npa})(N_3)(H_2O)]_n$ | 1D | 110.3 | 3.30 | 0.55 | 35.44 | this work |
| | 1Cu | $[Cu(p\text{-npa})(N_3)]_n$ | 2D | 120.4 | 3.39 | 0.40 | 52.25 | this work |
| | 1Cu | $[Cu(p\text{-mpa})(N_3)]_n$ | 2D | 122.4 | 3.46 | 0.53 | - | this work |

$J^a$ : intrachain coupling.

$L^1$ = $Me_3NCH_2CO_2$, Hpht = hydrogen phthalate, INO = isonicotinate *N*-oxide, NNO = nicotinate *N*-oxide, isonic = isonicotinate, phea = 1-phenylethylamine, nic = nicotinate, hnta = 6-hydroxynicotinate, tp = terephthalate, 4-Hpya = 4-pyridylacrylic acid, $L^2$ = 2-methyl-benzoate, *p*-CPAH = *p*-cyanophenoxyacetic acid, 2-Clnic = 2-chloronicotinate, pyz = pyrazine, mptz = *N*-methyl-4-pyridinium tetrazolate, 4,3-pybz = 4-(3-pyridyl)benzoate, 4,4-pybz = 4-(4-pyridyl)benzoate, Me-hmpz = 1-methylhomopiperazine, men = *N*-methylethylenediamine, *N*,*N*-dmen = *N*,*N*-dimethylethylenediamine, *N*,*N'*-dmen = *N*,*N'*-dimethylethylenediamine, $L^3$ is the imine resulting from the condensation of pyridine-2-carboxaldehyde with *N*-methylethylenediamine, $HL^4$ and $HL^5$ are the condensation products of 2-hydroxy-3-methoxybenzaldehyde with *N*,*N*-diethylethylenediamine and *N*-ethylethylenediamine respectively, *o*-Hnpa = *o*-nitrophenylacetic acid, *p*-Hnpa = *p*-nitrophenylacetic acid, and *p*-Hmpa = *p*-methylphenylacetic acid.

All of the *J* values were quoted using the Hamiltonian $\boldsymbol{H} = -J\sum S_i \bullet S_{i+1}$.




**(a)** **(b)** **(c)**

**Fig. S1** The coordination environments of Cu(II) ions in **1**(a), **2**(b) and **3**(c) respectively. H atoms and benzene rings have been omitted for clarity.

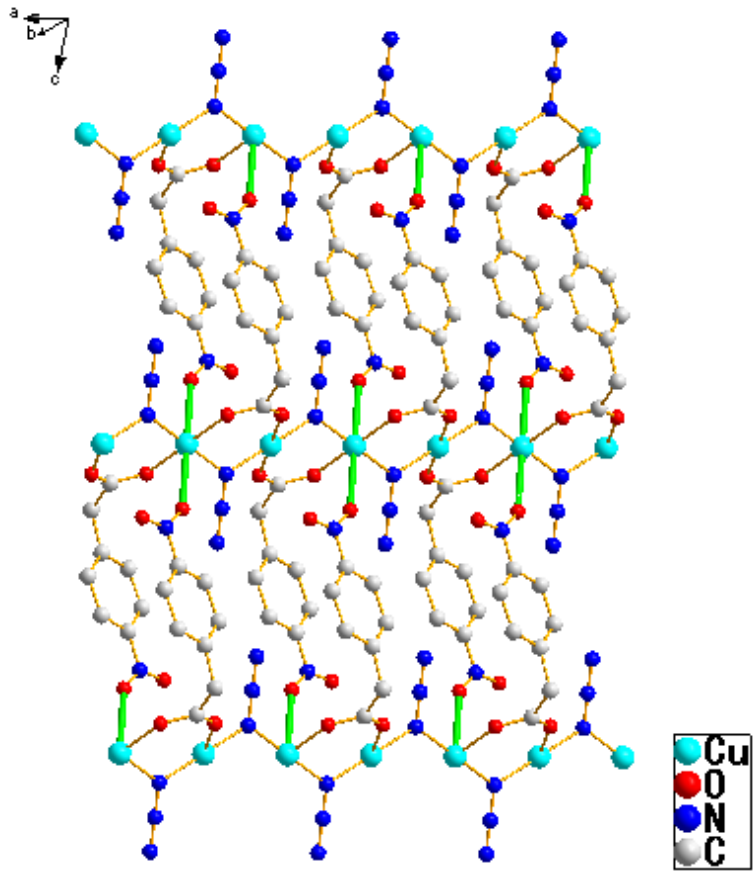
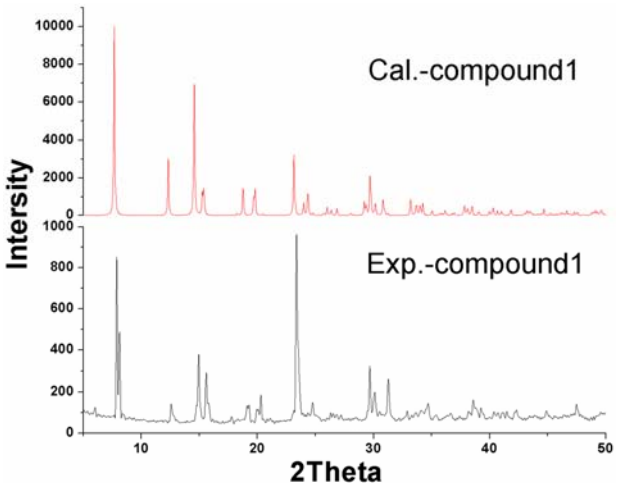
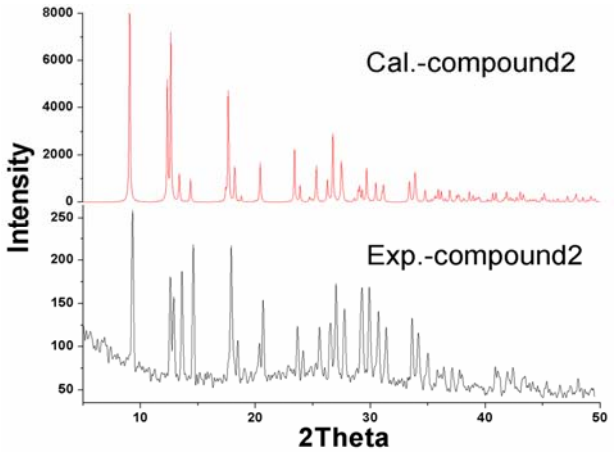


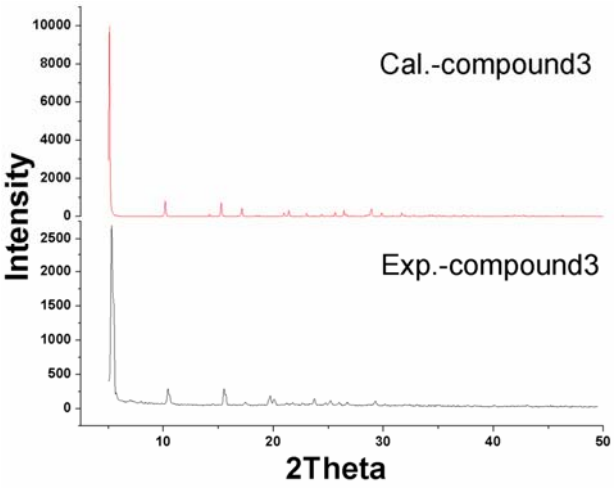

**Fig. S2** Two adjacent 1D chains are cross-linked by the coordinated nitro groups from the *p*-npa ligands forming the 2D structure of compound **2**. H atoms have been omitted for clarity.




**(a)**




**(b)**




**(c)**

**Fig. S3** The XRPD diagrams for compounds: (a) **1**, (b) **2**, and (c) **3**.

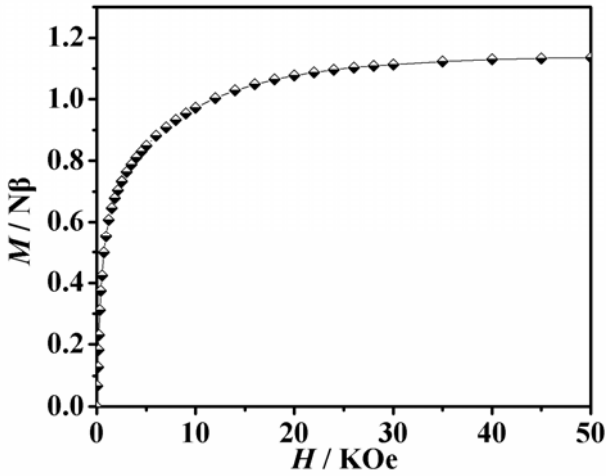



**Fig. S4** Magnetization *vs* H plot for compound **1**.

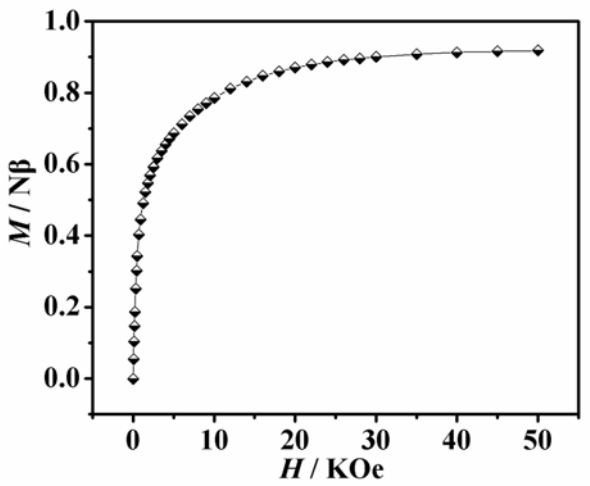



**Fig. S5** Magnetization *vs* H plot for compound **2**.

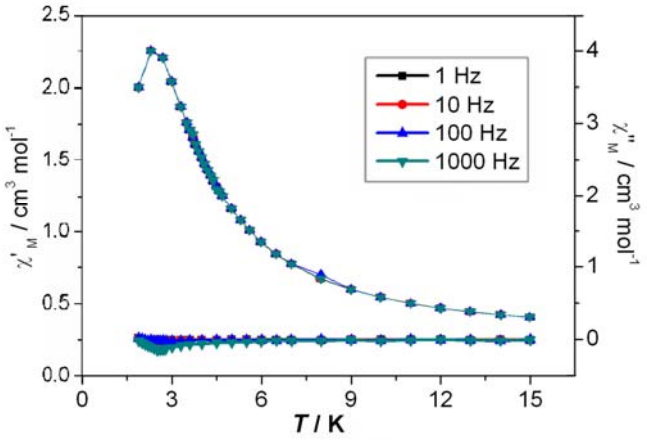



**Fig. S6** $\chi'_M$ and $\chi''_M$ *vs T* plots for compound **2**.

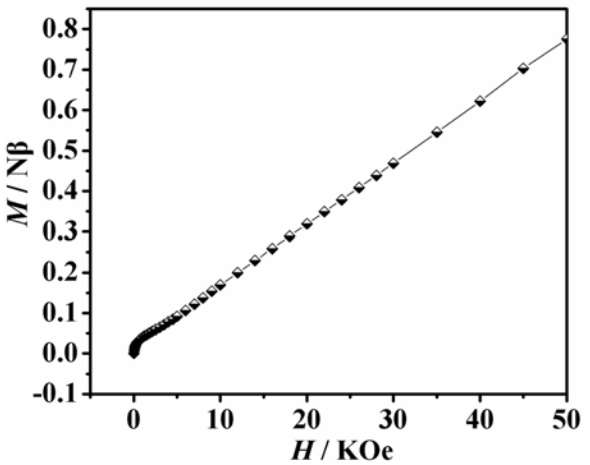



**Fig. S7** Magnetization *vs* H plot for compound **3**.