Supporting Information

Substituent effect of phenylacetic acid coligands perturbed structures and magnetic properties observed in two triple-bridged azido-Cu(II) chain compounds with ferromagnetic ordering and slow magnetic relaxation

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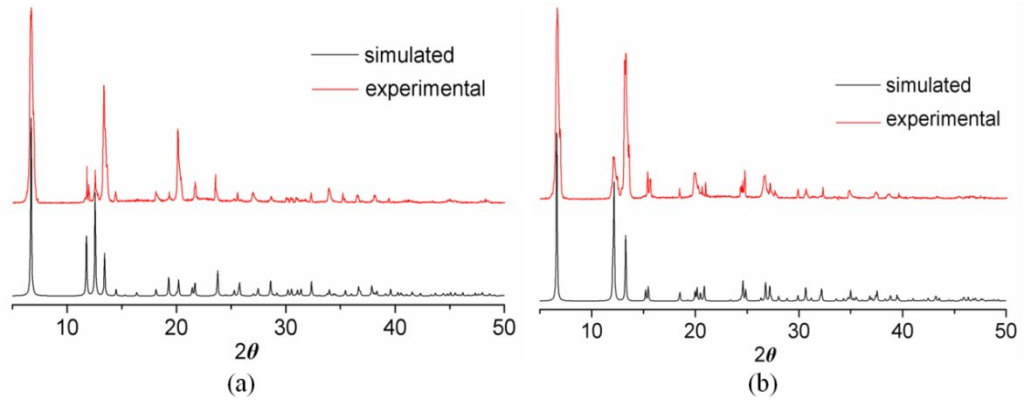

Fig. S1 PXRD patterns for compounds: (a) **1**, (b) **2**.

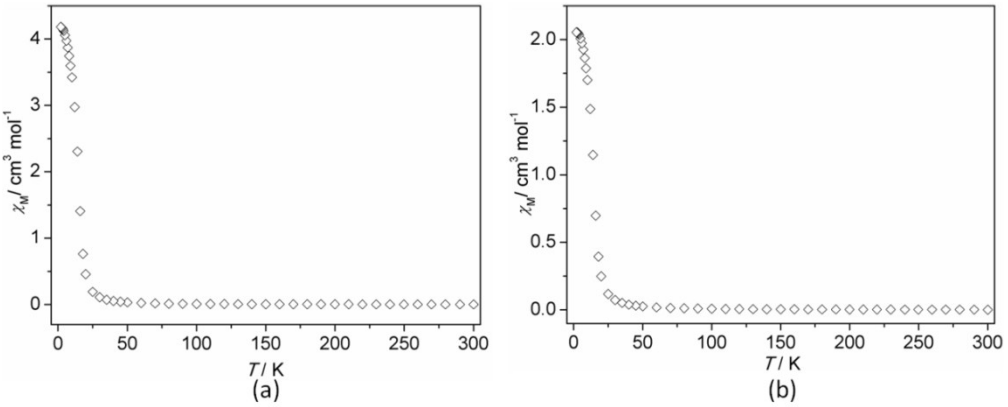

Fig. S2 χ_M *vs T* plots for **1** (a) and **2** (b).

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

1			
Cu(1)-O(1)	1.945(5)	O(2)-Cu(1)-O(1)	179.0(3)
Cu(1)-O(2)#1	1.942(5)	O(2)#1-Cu(1)-N(1)#1	91.4(2)
Cu(1)-O(3)	2.439(6)	O(1)-Cu(1)-N(1)#1	89.5(2)
Cu(1)-N(1)	2.007(8)	O(2)-Cu(1)-N(1)	89.1(2)
Cu(1)-N(1)#1	2.001(7)	O(1)-Cu(1)-N(1)	90.0(2)
N(1)-N(2)	1.198(6)	N(1)#1-Cu(1)-N(1)	176.3(3)
N(2)-N(3)	1.125(7)	C(1)-O(1)-Cu(1)	131.1(5)
O(3)-C(9)	1.433(9)	N(2)-N(1)-Cu(1)	122.6(7)
C(1)-O(1)	1.246(11)	C(9)-O(4)-Cu(1)	118.2(6)
C(1)-O(2)	1.266(11)	O(3)-Cu(1)-N(1)	99.8(2)
C(8)-F(1)	1.342(2)	N(3)-N(2)-N(1)	178.5(8)
#1 1-x,-1/2+y,1-z			

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

2			
Cu(1)-O(1)	1.935(6)	O(1)-Cu(1)-O(2)#1	179.0(3)
Cu(1)-O(2)	1.947(6)	O(1)-Cu(1)-N(1)#1	90.0(2)
Cu(1)-O(3)	2.427(7)	O(2)#1-Cu(1)-N(1)#1	90.4(3)
Cu(1)-N(1)	2.023(10)	O(1)-Cu(1)-N(1)	90.9(2)
Cu(1)-N(1)#1	1.975(10)	O(2)#1-Cu(1)-N(1)	88.8(2)
Cu(1)-O(3)#1	2.469(7)	N(1)#1-Cu(1)-N(1)	178.6(2)
N(1)-N(2)	1.206(6)	C(8)-O(1)-Cu(1)	127.8(5)
N(2)-N(3)	1.131(7)	N(2)-N(1)-Cu(1)#2	122.7(8)
F(1)-C(1)	1.36(3)	N(2)-N(1)-Cu(1)	119.0(9)
O(3)-C(9)	1.436(7)	Cu(1)#2-N(1)-Cu(1)	104.8(2)
C(8)-O(1)	1.279(13)	N(3)-N(2)-N(1)	178.0(9)
#1 1-x,-1/2+y,1-z	#2 1-x,1/2+y,1-z		

Table S3. The charge distributions of Cu(II) ions and coordination atoms for compounds **1** and **2**.

	1 (Natural charge c/m^3)	**2** (Natural charge c/m^3)
Cu1	1.30862	1.30011
Cu1A	1.31061	1.33218
O1 (carboxylates)	-0.73609	-0.73687
O1A (carboxylates)	-0.73067	-0.74645
N1	-0.71713	-0.74951
O2 (ethanol)	-0.73942	-0.77514

Table S4. Atomic spin densities (in au) for compounds **1** and **2** (for def2-tzvp basis set).

Atoms	**1**	**2**
Cu1	0.55850	0.55738
Cu1A	0.55945	0.57177
O1 (carboxylates)	0.07784	0.07921
O1A (carboxylates)	0.07571	0.08445
N1	0.07485	0.08472
O2 (ethanol)	0.00026	0.00004

Table S5. Structural and magnetic parameters for Cu(II)-azido mixed-bridged compounds.

Year	Unit	Formula	Cu-N-Cu(°)	Cu...Cu(Å) (intrachain)	J^a(cm^{-1})	Ref.
1997	2Cu	$[Cu_2(N_3)_2(NO_3)_2(L^1)_2]_n$	119.5	3.44	26	15b
	1Cu	$\{[Cu(Hpht)(N_3)]H_2O\}_n$	111.9	3.28	75	15*a*
2006	1Cu	$[Cu(INO)(N_3)(H_2O)_{0.5}]_n$	106.6	3.22	80	33*c*
	1Cu	$[Cu(NNO)(N_3)(H_2O)_{0.5}]_n$	124.3	3.52	48	33*c*
	1.5Cu	$[Cu_{1.5}(N_3)_2(isonic)]_n$	106.7	3.20	80	34*a*
2007	3Cu	$[Cu_3((R)\text{-}phea)_2(N_3)_6]_n$	101.8	3.04	15.27	34*b*
	3Cu	$[Cu_3((S)\text{-}phea)_2(N_3)_6]_n$				
	1Cu	$[Cu(N_3)(nic)]_n$	113.6	3.35	39.1	34*c*
	1.5Cu	$[Cu_{1.5}(hnta)(N_3)_2(H_2O)]_n$	103.2	3.12	89	29*b*
	3Cu	$[Cu_3(hnta)_4(N_3)_2(H_2O)_3]_n$	116.2	3.39	69.7	29*b*
2008	1Cu	$[Cu(N_3)(tp)(CH_3OH)]_n$	105.5	3.19	63	34*d*
2009	2Cu	$[Cu_2(4\text{-}pya)_2(N_3)_2(DMF)]_n$	102.1	-	145	33*b*
	1Cu	$[Cu(benzoate)(N_3)]_n$	126.8	3.54	33.90	18*a*
	1Cu	$[Cu(L^2)(N_3)]_n$	108.2	3.23	93.10	18*a*
	1Cu	$[Cu(1\text{-}naphthoate)(N_3)]_n$	116.8	3.41	65.63	18*a*
	1Cu	$[Cu(N_3)(p\text{-}CPA)]_n$	107.0	3.18	68.82	35*a*
2010	1Cu	$[Cu(2\text{-}Clnic)(N_3)(CH_3OH)]_n$	110.3	3.29	81.22	35*b*
	3Cu	$[Cu_3(pyz)_2(N_3)_6]_n$	100.5	3.09	118.8	35*c*

2011	1Cu	$[Cu(mptz)(N_3)_2]_n$	103.3	3.15	65.4	35*d*
	1Cu	$[Cu(4,3\text{-pybz})(N_3)]_n$	109.4	3.25	63.9	18*b*
	2Cu	$[Cu_2(4,4\text{-pybz})_3(N_3)]_n \cdot 3nH_2O$	101.1	3.08	93.6	18*b*
2012	4Cu	$[Cu_4(N_3)_8(Me\text{-hmpz})_2]_n$	101.0	3.11	J_1=40.57 J_2=28.47	35*e*
	4Cu	$[Cu_4(N_3)_8(men)_2]_n$	102.2	3.40	J_1=57.97 J_2=-14.03	35*e*
	5Cu	$[Cu_5(N_3)_{10}(N,N\text{-dmen})_2]_n$	101.6	3.40	J_1=-494.99 J_2=88.60	35*e*
	5Cu	$[Cu_5(N_3)_{10}(N,N'\text{-dmen})_5]_n$	102.2	3.50	-	35*e*
2013	4Cu	$[Cu_4(N_3)_8(L^3)_2]_n$	102.9 137.1	3.12 4.13	J_1=-0.70 J_2=64.9	35*f*
	4Cu	$[Cu_4(N_3)_6(L^4)_2(H_2O)_2]$	93.4 102.1 108.9	3.10 3.22	J_1=-81.0 J_2=112.4	35*f*
	4Cu	$[Cu_4(N_3)_6(L^5)_2]_n$	91.8 102.2 107.3	3.18 3.09 3.18	J_1=-77.9 J_2=129.9	35*f*
2014	1Cu	$[Cu(4\text{-fba})(N_3)(C_2H_5OH)]$	105.2	3.160	36.2	9*f*
	1Cu	$[Cu(o\text{-npa})(N_3)(H_2O)]n$	110.3	3.30	35.44	9*g*
	1Cu	$[Cu(p\text{-npa})(N_3)]n$	120.4	3.39	52.25	9*g*
	1Cu	$[Cu(p\text{-mpa})(N_3)]n$	122.4	3.46	-	9*g*
2015	1Cu	$[Cu(L)(N_3)]_2$	89.8	3.199	1.07	36*a*
2016	1Cu	$[(CuN_3(OH_2))_2(adp)]_n$	108.09	3.248	38.4	36*b*
2017	1Cu	$[Cu(2\text{-fba})(N_3)(CH_3OH)]_n$	106.54	3.206	63.54	37
	1Cu	$[Cu(2,6\text{-dfba})(N_3)(CH_3OH)]_n$	110.08	3.261	96.29	37
	1Cu	$[Cu(o\text{-fpa})(N_3)(C_2H_5OH)]_n$	106.8	3.218	87.08	This work
	1Cu	$[Cu(p\text{-fpa})(N_3)(C_2H_5OH)]_n$	104.8	3.168	66.05	This work

J^a : intrachain coupling.

L1 = $Me_3NCH_2CO_2$, 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, 4-Hfba = 4-fluorobenzoic acid, *o*-Hfpa = *o*-fluorophenylacetic acid, *p*-Hfpa = *p*-fluorophenylacetic acid, L = N-benzyl ethylenediamine, adp = adipic acid, 2-Hfba = 2-fluorobenzoic acid, 2,6-Hdfba = 2,6-difluorobenzoic acid, *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 $H = -J\sum S_i \cdot S_{i+1}$.

Table S6. Structural and magnetic parameters for four triple-bridged azido-Cu(II) compounds.

Formula	Cu-N-Cu(°)	Cu-Cu (Å) (intrachain)	Hydrogen-bonding (Å) (interchain)	Cu...Cu (Å) (interchain)	J^a(cm^{-1})	Ref.
$[Cu(o\text{-fpa})(N_3)(C_2H_5OH)]_n$	106.8	3.218	2.901	7.615	87.08	This work
$[Cu(p\text{-fpa})(N_3)(C_2H_5OH)]_n$	104.8	3.168	2.902	7.562	66.05	This work
$[Cu(2\text{-fba})(N_3)(CH_3OH)]_n$	106.6	3.206	2.861	7.512	63.54	37
$[Cu(2,6\text{-dfba})(N_3)(CH_3OH)]_n$	110.3	3.266	2.927	7.784	96.29	37