Supporting Information

Solvent-induced single-crystal-to-single-crystal transformation and tunable magnetic property of 1D azido-Cu(II) chains with carboxylate bridge

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Contents

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Table S1. Selected bond lengths (Å) and bond angles (°) for **1**-**3**.

1		**2**		**3**	
Cu(1)-O(1)#1	1.966(5)	Cu(1)-O(1)	1.957(7)	Cu(1)-O(2)	1.954(4)
Cu(1)-O(1)	1.966(5)	Cu(1)-O(1)#1	1.957(7)	Cu(1)-O(1)	1.962(4)
Cu(1)-N(1)#1	1.985(6)	Cu(1)-N(1)	1.998(9)	Cu(1)-N(1)#1	1.992(5)
Cu(1)-N(1)	1.985(6)	Cu(1)-N(1)#1	1.998(9))	Cu(1)-N(1)	1.995(5)
O(1)-C(6)	1.274(9)	Cu(1)-O(3)	2.495(8)	Cu(1)-O(3)	2.419(4)
O(2)-C(6)	1.256(9)	Cu(1)-O(3)#1	2.515(8)	Cu(1)-O(3)#1	2.513(4)
N(1)-N(2)	1.228(9)	O(1)-C(1)	1.300(13)	O(1)-C(1)	1.257(7)
N(2)-N(3)	1.150(9)	O(2)-C(1)	1.289(13)	C(1)-O(2)#1	1.259(7)
N(4)-N(5)	1.253(9)	O(3)-C(8)	1.414(16)	N(5)-N(6)	1.106(11)
C(3)-C(13)	1.398(10)	N(1)-N(2)	1.195(12)	N(5)-N(4)	1.253(11)
C(3)-C(12)	1.404(10)	N(2)-N(3)	1.174(13)	N(1)-N(2)	1.234(7)
C(3)-C(6)	1.485(9)	N(4)-N(5)	1.29(2)	N(2)-N(3)	1.115(7)
O(1)#1-Cu(1)-O(1)	180.0(3)	O(1)-Cu(1)-O(1)#1	180.0(4)	O(2)-Cu(1)-O(1)	177.78
O(1)#1-Cu(1)-N(1)#1	88.2(2)	O(1)-Cu(1)-N(1)	91.3(3)	O(2)-Cu(1)-O(1)	90.65(19)
O(1)-Cu(1)-N(1)#1	91.8(2)	O(1)#1-Cu(1)-N(1)	88.7(3)	O(1)-Cu(1)-N(1)#1	90.54(19)
O(1)#1-Cu(1)-N(1)	91.8(2)	O(1)-Cu(1)-N(1)#1	88.7(3)	O(2)-Cu(1)-N(1)	89.42(19)
O(1)-Cu(1)-N(1)	88.2(2)	O(1)#1-Cu(1)-N(1)#1	91.3(3)	O(1)-Cu(1)-N(1)	89.51(19)
N(1)#1-Cu(1)-N(1)	180.0	N(1)-Cu(1)-N(1)#1	180.0	N(1)#1-Cu(1)-N(1)	176.20(1)
O(2)#1-Cu(2)-O(2)#2	91.2(2)	O(1)-Cu(1)-O(3)	87.2(3)	O(2)-Cu(1)-O(3)	91.87(18)
O(2)#2-Cu(2)-N(1)	88.8(2)	O(1)#1-Cu(1)-O(3)	92.8(3)	O(1)-Cu(1)-O(3)	86.34(17)
O(2)#1-Cu(2)-N(1)#3	88.8(2)	N(1)-Cu(1)-O(3)	84.4(3)	N(1)#1-Cu(1)-O(3)	86.63(18)
O(2)#2-Cu(2)-N(1)#3	91.2(2)	N(1)#1-Cu(1)-O(3)	95.6(3)	N(1)-Cu(1)-O(3)	97.16(17)
N(1)-Cu(2)-N(1)#3	180.0	O(2)#2-Cu(2)-O(2)	180.0(4)	C(1)-O(1)-Cu(1)	129.7(4)
C(6)-O(1)-Cu(1)	134.2(5)	O(2)#2-Cu(2)-N(1)	89.3(3)	O(1)-C(1)-O(2)#1	127.4(5)
C(6)-O(2)-Cu(2)#4	131.2(5)	O(2)-Cu(2)-N(1)	90.7(3)	O(1)-C(1)-C(2)	116.3(5)
N(2)-N(1)-Cu(1)	119.3(5)	O(2)#2-Cu(2)-N(1)#2	90.7(3)	N(2)-N(1)-Cu(1)#2	120.7(4)
N(2)-N(1)-Cu(2)	113.5(5)	O(2)-Cu(2)-N(1)#2	89.3(3)	N(2)-N(1)-Cu(1)	119.7(4)
Cu(1)-N(1)-Cu(2)	127.2(3)	N(1)-Cu(2)-N(1)#2	180.0	Cu(1)#2-N(1)-Cu(1)	104.5(2
N(3)-N(2)-N(1)	179.0(9)	N(3)-N(2)-N(1)	176.1(16)	N(3)-N(2)-N(1)	176.4(9)
N(6)-N(5)-N(4)	116.3(7)	N(6)-N(5)-N(4)	174(2)	C(8)-O(3)-Cu(1)	124.8(4)
#1 -x+1,-y+2,-z+1 #2 x,y-1,z		#1 -x,-y+1,-z+1		#1-x+1/2,y+1/2,-z+1/2	
#3 -x+1,-y+1,-z+1 #4 x,y+1,z		#2 -x+1,-y+1,-z+1		#2 -x+1/2,y-1/2,-z+1/2	

Table S2. Structural and magnetic parameters for Cu(II)-azido mixed-bridged compounds.

Unit	Formula	Cu-N-Cu(°)	Cu...Cu(Å) (intrachain)	J^a(cm^{-1})	Ref.
2Cu	$[Cu_2(N_3)_2(NO_3)_2(L^1)_2]_n$	119.5	3.44	26	1

1Cu	$\{[Cu(Hpht)(N_3)]H_2O\}_n$	111.9	3.28	75	2
1Cu	$[Cu(INO)(N_3)(H_2O)_{0.5}]_n$	106.6	3.22	80	3
1Cu	$[Cu(NNO)(N_3)(H_2O)_{0.5}]_n$	124.3	3.52	48	3
1.5Cu	$[Cu_{1.5}(N_3)_2(isonic)]_n$	106.7	3.20	80	4
3Cu	$[Cu_3((R)\text{-phea})_2(N_3)_6]_n$	101.8	3.04	15.27	5
3Cu	$[Cu_3((S)\text{-phea})_2(N_3)_6]_n$				
1Cu	$[Cu(N_3)(nic)]_n$	113.6	3.35	39.1	6
1.5Cu	$[Cu_{1.5}(hnta)(N_3)_2(H_2O)]_n$	103.2	3.12	89	7
3Cu	$[Cu_3(hnta)_4(N_3)_2(H_2O)_3]_n$	116.2	3.39	69.7	7
1Cu	$[Cu(N_3)(tp)(CH_3OH)]_n$	105.5	3.19	63	8
2Cu	$[Cu_2(4\text{-pya})_2(N_3)_2(DMF)]_n$	102.1	-	145	9
1Cu	$[Cu(benzoate)(N_3)]_n$	126.8	3.54	33.90	10
1Cu	$[Cu(L^2)(N_3)]_n$	108.2	3.23	93.10	10
1Cu	$[Cu(1\text{-naphthoate})(N_3)]_n$	116.8	3.41	65.63	10
1Cu	$[Cu(N_3)(p\text{-CPA})]_n$	107.0	3.18	68.82	11
1Cu	$[Cu(2\text{-Clnic})(N_3)(CH_3OH)]_n$	110.3	3.29	81.22	12
3Cu	$[Cu_3(pyz)_2(N_3)_6]_n$	100.5	3.09	118.8	13
1Cu	$[Cu(mptz)(N_3)_2]_n$	103.3	3.15	65.4	14
1Cu	$[Cu(4,3\text{-pybz})(N_3)]_n$	109.4	3.25	63.9	15
2Cu	$[Cu_2(4,4\text{-pybz})_3(N_3)]_n \cdot 3nH_2O$	101.1	3.08	93.6	15
4Cu	$[Cu_4(N_3)_8(Me\text{-hmpz})_2]_n$	101.0	3.11	J_1=40.57 J_2=28.47	16
4Cu	$[Cu_4(N_3)_8(men)_2]_n$	102.2	3.40	J_1=57.97 J_2=-14.03	16
5Cu	$[Cu_5(N_3)_{10}(N,N\text{-dmen})_2]_n$	101.6	3.40	J_1=-494.99 J_2=88.60	16
5Cu	$[Cu_5(N_3)_{10}(N,N'\text{-dmen})_5]_n$	102.2	3.50	-	16
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	17

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	17
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	17
1Cu	$[Cu(4\text{-fba})(N_3)(C_2H_5OH)]$	105.2	3.160	36.2	18
1Cu	[Cu(*o*-npa)$(N_3)(H_2O)$]n	110.3	3.30	35.44	19
1Cu	[Cu(*p*-npa)(N_3)]n	120.4	3.39	52.25	19
1Cu	[Cu(*p*-mpa)(N_3)]n	122.4	3.46	-	19
1Cu	$[Cu(L)(N_3)]_2$	89.8	3.199	1.07	20
1Cu	$[(CuN_3(OH_2))_2(adp)]_n$	108.09	3.248	38.4	21
1Cu	$[Cu(2\text{-fba})(N_3)(CH_3OH)]_n$	106.54	3.206	63.54	22
1Cu	$[Cu(2,6\text{-dfba})(N_3)(CH_3OH)]_n$	110.08	3.261	96.29	22
1Cu	$[Cu(o\text{-fpa})(N_3)(C_2H_5OH)]_n$	106.8	3.218	87.08	23
1Cu	$[Cu(p\text{-fpa})(N_3)(C_2H_5OH)]_n$	104.8	3.168	66.05	23
1Cu	$[\{Cu(2\text{-ap})(N_3)_2(H_2O)\}_2]_n$	103.3	3.20	66.7	24
3Cu	$[Cu_3(3\text{-ap})_2(N_3)_6]_n$	101.3 102.2 99.0	3.01	J_1=30 J_2=67	24
1Cu	$[Cu(3\text{-fba})(N_3)(C_2H_5OH)]_n$	105.95	3.192	59.74	25
2Cu	$[Cu_2(ip_2en)_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$	101.77 102.51	3.3526	7.0	26
1Cu	catena-$[Cu(ambza)(\mu_{1,1,3}\text{-}N_3)_2]$	99.64	3.4103	7.7	26
1Cu	$[Cu(4\text{-tfmba})(N_3)(CH_3OH)]$	107.04	3.213	56.21	27
1Cu	$[Cu(4\text{-tfmba})(N_3)(C_2H_5OH)]$	106.53	3.180	68.94	27
1Cu	$[Cu(4\text{-tfmba})(N_3)(C_3H_7OH)]$	107.93	3.205	77.94	27

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, 2-ap = 2-aminopyridine, 3-ap = 3-aminopyridine, and 4-ap = 4-aminopyridine, 3-fba = 3-fluorobenzoic acid, Et_3en = *N*,*N*,*N* -triethyl-1,2-diaminoethane; ip_2en = *N*,*N*'-diisopropyl-1,2-diaminoethane; Et_2Meen = *N*,*N* -diethyl- *N*'-methyl-1,2-diaminoethane; and ambza = 2-aminobenzylamine, H_2L^1 = *N*,*N*-bis(3,5-dimethyl-2-hydroxybenzyl)-*N',N'*-dimethyl-1,3-diaminopropane, H_2L^2 = *N*,*N*-bis(3,5-dimethyl-2-hydroxybenzyl)-*N',N'*-dimethyl-1,2-diaminoethane and H_2L^3 = *N*,*N*-bis(3,5-dimethyl-2-hydroxybenzyl)-*N',N*'-diethyl-1,2-diaminoethane, L = *N*,*N*-dimethyl-*N*'-benzyl-ethylenediamine, 4-tfmba = 4-trifluoromethyl benzoic acid.

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

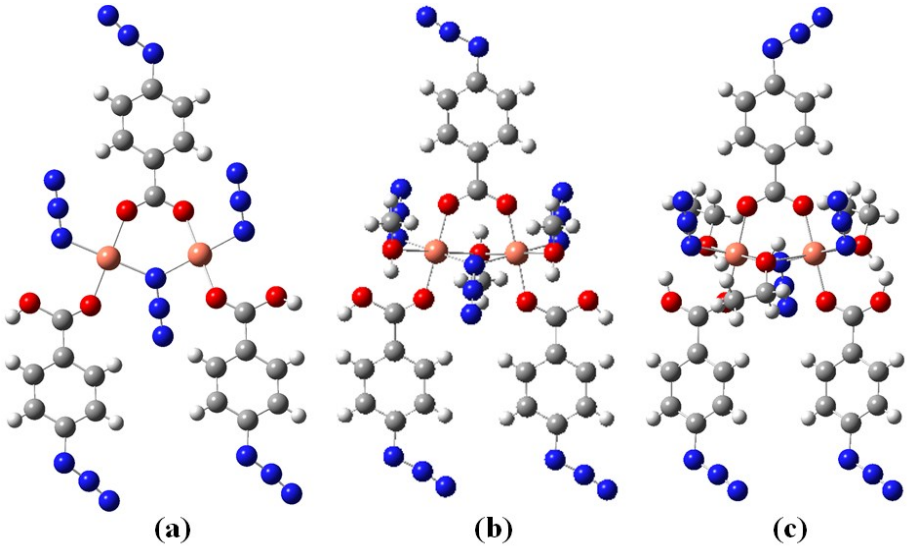

Figure S1. Magnetic cores used for computational study: (a) **1**, (b) **2**, (c) **3**.

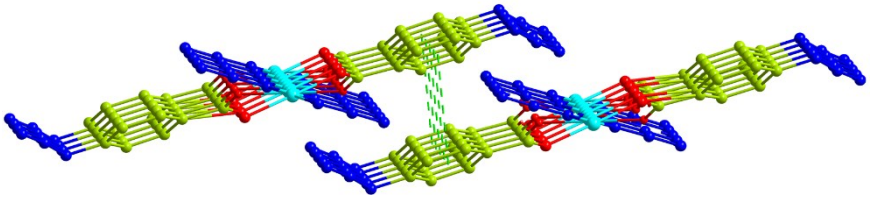

Figure S2. π···π stacking between benzene rings in **1**.

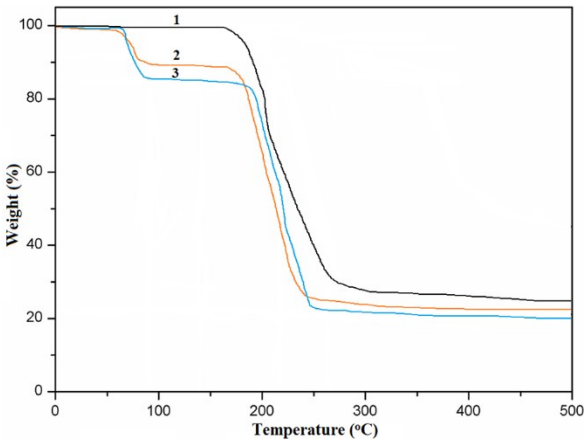

Figure S3. TG curves for **1**-**3**.

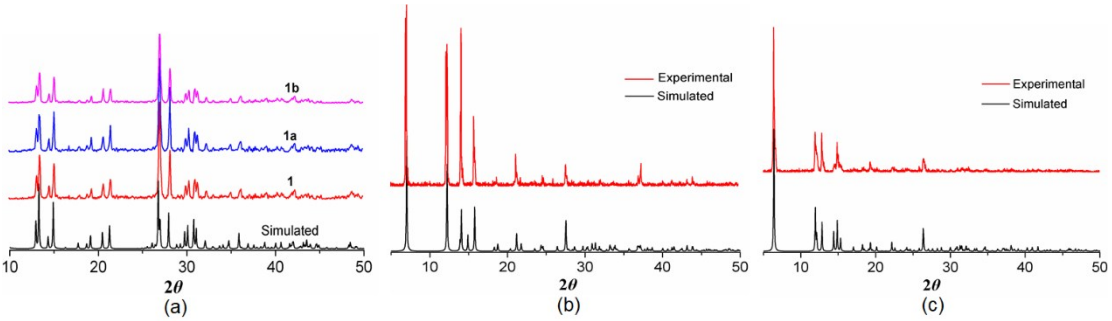

Figure S4. PXRD patterns for compounds: (a) **1**, (b) **2**, (c) **3**.

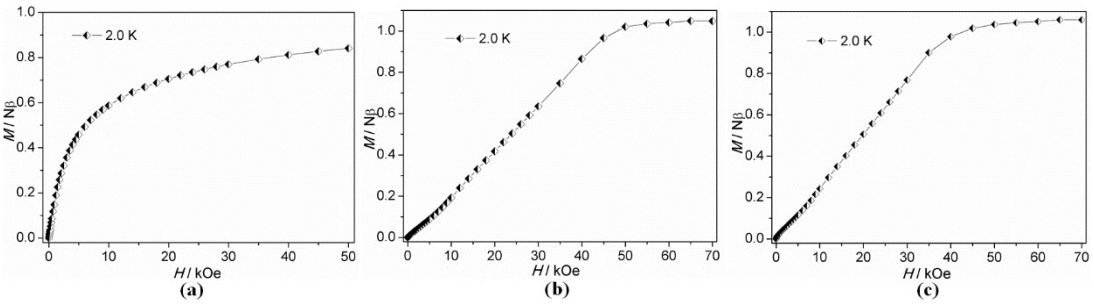

Figure S5. (a) *M vs*. *H* plots at 2 K for compounds: (a) **1**, (b) **2**, (c) **3**.

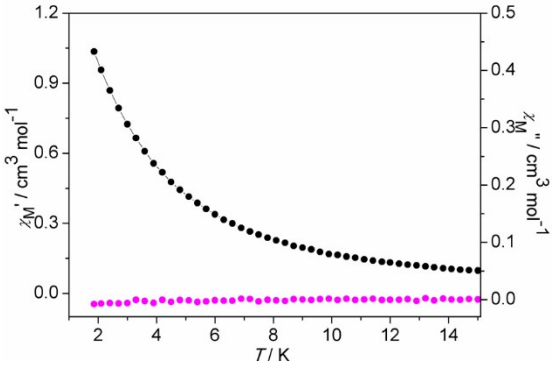

Figure S6. χ'_M and χ''_M *vs* *T* plots for **1**.

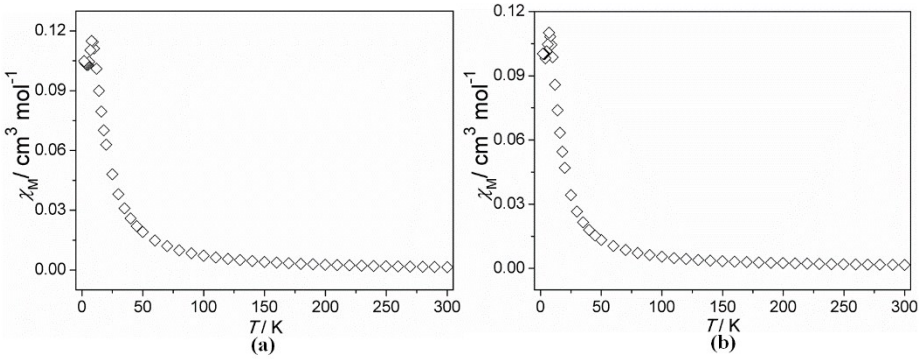

Figure S7. χ_M *vs* T plots for **2** (a) and **3** (b).

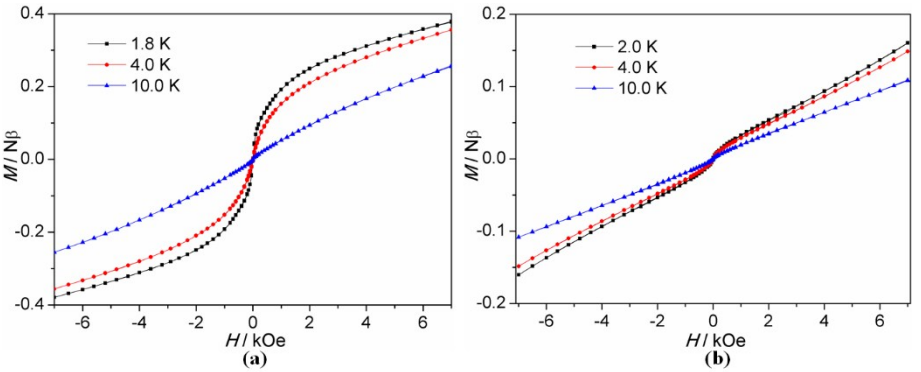

Figure S8. (a) Hysteresis loops for **2** (a) and **3** (b) at different temperatures.

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