Supporting Information

Solvent coligands fine-tuned the structures and magnetic properties of triple-bridged 1D azido-copper(II) coordination polymers

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

1		**2**		**3**	
Cu(1)-O(1)	1.939(5)	Cu(1)-O(2)	1.944(5)	Cu(1)-O(1)	1.952(6)
Cu(1)-O(1)#1	1.939(5)	Cu(1)-O(2)#1	1.944(5)	Cu(1)-O(1)#1	1.952(6)
Cu(1)-N(1)	1.988(6)	Cu(1)-N(1)	1.983(7)	Cu(1)-N(1)	1.970(7)
Cu(1)-N(1)#1	1.988(6)	Cu(1)-N(1)#1	1.983(7)	Cu(1)-N(1)#1	1.970(7)
Cu(1)-O(3)	2.503(6)	Cu(1)-O(3)	2.511(6)	Cu(1)-O(3)	2.579(7)
Cu(2)-O(2)	1.952(5)	Cu(2)-O(1)	1.949(5)	Cu(2)-O(2)	1.959(6)
Cu(2)-O(2)#2	1.952(5)	Cu(2)-O(1)#2	1.949(5)	Cu(2)-O(2)#2	1.959(6)
Cu(2)-N(1)#2	2.009(6)	Cu(2)-N(1)#2	1.987(6)	Cu(2)-N(1)#2	1.995(7)
Cu(2)-N(1)	2.009(6)	Cu(2)-N(1)	1.987(6)	Cu(2)-N(1)	1.995(7)
Cu(2)-O(3)	2.518(6)	Cu(1)-Cu(2)	3.180(6)	Cu(2)-O(3)	2.515(6)
O(1)#1-Cu(1)-O(1)	180.000(1)	O(2)-Cu(1)-O(2)#1	180.0(15)	O(1)#1-Cu(1)-O(1)	180.000(1)
O(1)#1-Cu(1)-N(1)	89.7(2)	O(2)-Cu(1)-N(1)#1	89.5(2)	O(1)#1-Cu(1)-N(1)	89.7(3)
O(1)-Cu(1)-N(1)	90.3(2)	O(1)-Cu(2)-O(1)#2	180.0(2)	O(1)-Cu(1)-N(1)	90.3(3)
O(1)#1-Cu(1)-O(3)	94.0(2)	Cu(2)-O(3)-Cu(1)	79.18(17)	O(1)#1-Cu(1)-O(3)	94.5(2)
O(1)-Cu(1)-O(3)	86.0(2)	Cu(1)-N(1)- Cu(2)	106.5(3)	O(1)-Cu(1)-O(3)	85.5(2)
#1-x+1,-y+2,-z		#1 -x+1,-y+1,-z+1		#1 -x+1,-y,-z+1	
#2-x,-y+2,-z		#2 -x,-y+1,-z+1		#2 -x,-y,-z+1	

Table S2. Hydrogen bonding interactions in **1**-**3**.

compound	Hydrogen bonding interactions				
1	D-H...A	d(D-H)	d(H...A)	d(D...A)	＜(DHA)
	O(3)-H(2)...N(3)#3	0.98	1.92	2.879(10)	166.6
	#1 -x+1,-y+2,-z	#2 -x,-y+2,-z	#3 x,y-1,z		
2	D-H...A	d(D-H)	d(H...A)	d(D...A)	＜(DHA)
	O(3)-H(5)...N(3)#3	0.79(13)	2.13(13)	2.907(10)	171(14)
	#1 -x+1,-y+1,-z+1	#2 -x,-y+1,-z+1	#3 x,y+1,z		
3	D-H...A	d(D-H)	d(H...A)	d(D...A)	＜(DHA)
	O(3)-H(1)...N(3)#3	0.80(2)	2.17(3)	2.952(12)	169(14)
	#1 -x+1,-y,-z+1	#2 -x,-y,-z+1	#3 x,y+1,z		

Table S3. Comparisons of the experimental fitting and DFT calculation

		BP86			B3LYP		
		def2-tzvp	tzvp	tzv	def2-tzvp	tzvp	tzv
1	E_{HS}/eV	-174025.35876	-174021.42304	-173996.23780	-173965.15105	-173961.04925	-173933.95464
	E_{BS}/eV	-174025.35021	-174021.41438	-173996.22992	-173965.14269	-173961.04097	-173933.94696
	J_{DFT}/cm^{-1}	68.71	69.65	63.28	67.36	66.74	61.88
	J_{Expt}/cm^{-1}	56.21					
2	E_{HS}/eV	-177222.94492	-177218.88028	-177192.23842	-177160.62292	-177156.38115	-177127.77325
	E_{BS}/eV	-177222.93580	-177218.87107	-177192.23025	-177160.61289	-177156.37122	-177127.76399
	J_{DFT}/cm^{-1}	73.12	73.87	65.41	80.79	80.05	74.52
	J_{Expt}/cm^{-1}	68.94					
3	E_{HS}/eV	-180439.71763	-180435.65888	-180408.67120	-180375.55046	-180371.31005	-180342.16398
	E_{BS}/eV	-180439.70670	-180435.64794	-180408.66105	-180375.53956	-180371.29931	-180342.15392
	J_{DFT}/cm^{-1}	87.98	88.09	81.57	87.79	86.53	81.03
	J_{Expt}/cm^{-1}	77.94					

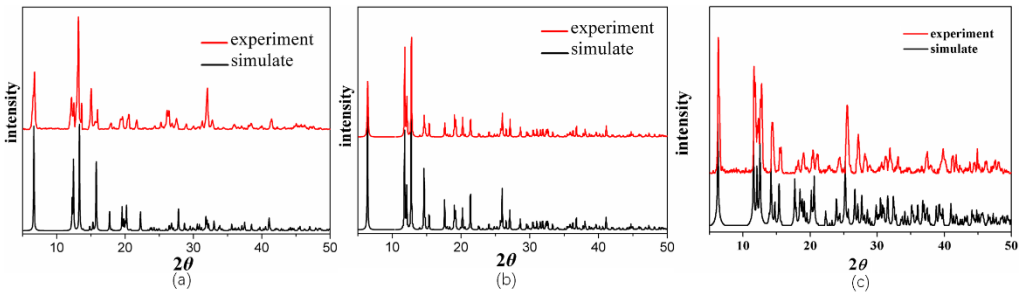

Figure S1. PXRD patterns for compounds: **1** (a), **2** (b), **3** (c).

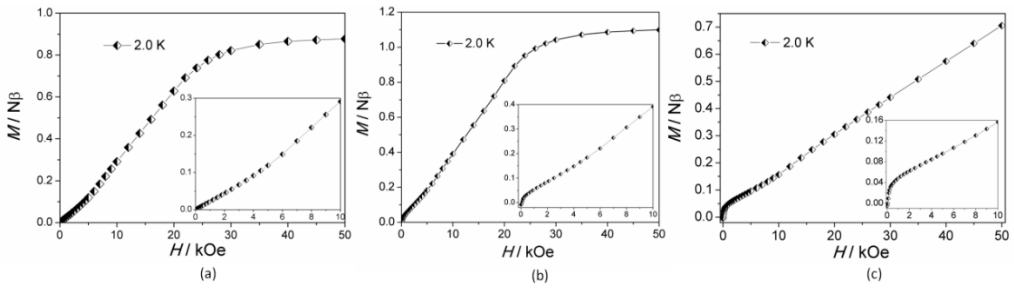

Figure S2. *M* versus *H* plots at 2.0 K for compounds **1** (a), **2** (b) and **3** (c).

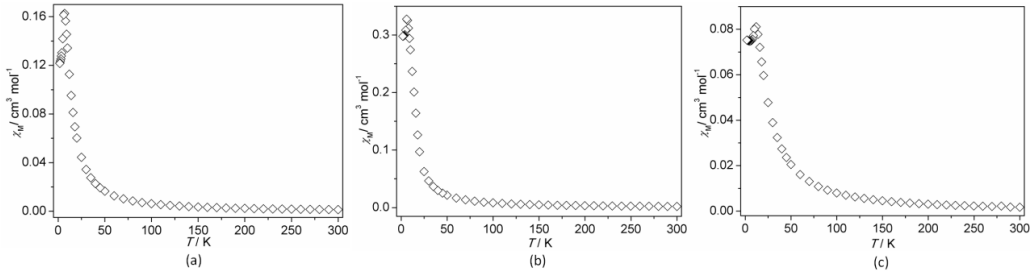

Figure S3. The temperature dependences of χ_M curves for **1**-**3**.

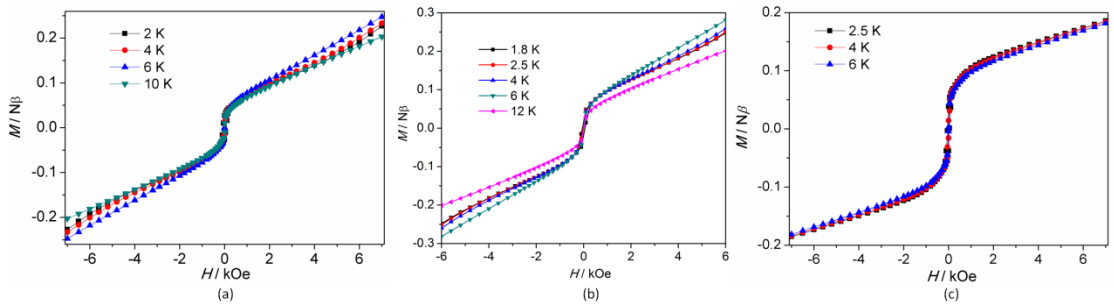

Figure S4. *M* vs *H* curves for compounds **1** (a), **2** (b) and **3** (c) at different temperatures.

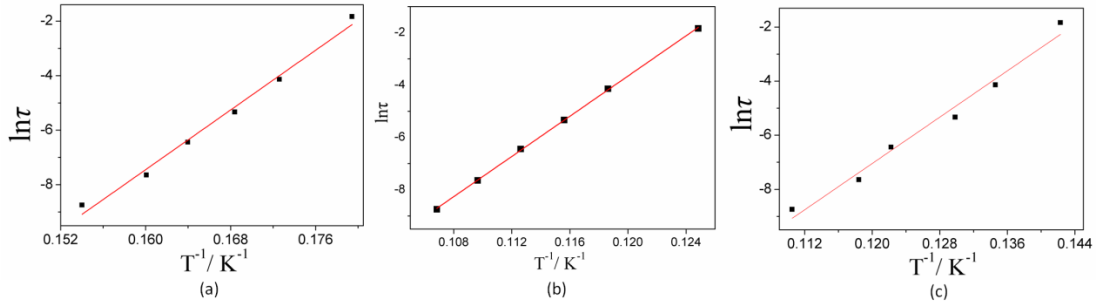

Figure S5. Plots of relaxation time (ln τ) vs T^{-1} for **1** (a), **2** (b) and **3** (c) at zero dc field. The red line is fitted with the Arrhenius law.

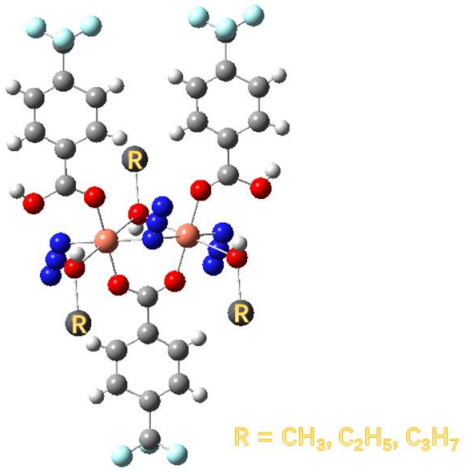

Figure S6. Magnetic cores of **1** (a), **2** (b) and **3** (c) used for computational study.