Solvent-Induced Structural Transformation and Magnetic Modulation in 1D Copper (II) Polymers Based on a Semi-rigid Ligand Containing 4amino-1,2,4-triazole

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1. Experimental Section

Commercially available reagents were used as received without further purification. The intermediate 4-amino-5-(quinolin-6-yl)-(4*H*)-1,2,4-triazole-3-thiol (**A**) was prepared by following a procedure in literature.¹ Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400-4000 cm⁻¹ range using a Perkin-Elmer 1600 FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer Model 2400 analyzer. Thermogravimetric analyses were carried out using a TA Instrument SDT 2960 simultaneous DTA-TGA under flowing nitrogen at a heating rate of 10 °C/min. ¹H NMR data were collected using an AM-300 spectrometer. Chemical shifts are reported in δ relative to TMS. Powder X-ray diffraction (PXRD) patterns were obtained at 293 K on a D8 ADVANCE (Cu K α 1, λ = 1.54056 Å; K α 2, λ = 1.54439 Å). The crystalline powder samples were prepared by crushing the crystals and the PXRD scanned from 5 to 50° at a rate of 5° min⁻¹. Calculated PXRD patterns were generated using Mercury 3.8. Magnetization measurements for polycrystalline samples were performed on a Quantum Design MPMS-SQUID-VSM magnetometer in the temperature range from 2 to 300 K for direct current (dc) applied fields 1000 Oe.

Preparation of L.

A solution of **A** (1.22 g, 5 mmol), 3-(chloromethyl)pyridine hydrochloride (0.98 g, 6 mmol), K_2CO_3 (6.9 g, 50 mmol) and a catalytic amount of KI in DMF (30 mL) was stirred for 24 hours. Then, the resulted mixture was poured into icy water. The precipitation was collected by filtration, washed with water and dried. The obtained sample was purified by column (dichloromethane: methanol, 20:1, v/v) to generate white solids 1.16 g (Yield, 67.8 %). M.P. 190-192 °C. ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C, TMS, ppm): 8.96-8.97 (d, 1H, -C₅H₃N); 8.67-8.69 (d, 1H, -C₆H₃); 8.43-8.45 (d, 2H, -C₅H₄N); 8.32-8.35 (d, 1H, -C₅H₃N); 8.11-8.14 (m, 2H, -C₅H₄N); 7.88-7.90 (d, 1H, -C₆H₃); 7.58-7.63 (d, 1H, -C₆H₃); 7.34-7.38 (d, 1H, -C₅H₃N); 6.26 (s, 2H, -NH₂); 4.49 (s, 2H, -CH₂-). IR (KBr, pellet, cm⁻¹⁾: 3276(w), 3169(w), 1626 (w), 1571 (w), 1470 (m), 1398 (m), 1289 (w), 1088 (m), 897 (s), 849 (w), 709 (s), 637 (w), 480 (w). Elemental analysis Calcd (%) for C₁₇H₁₄N₆S: C 61.06, H 4.22, N 25.13; Found: C 61.17, H 4.18, N 25.46.

Preparation of [Cu(L)Br₂(CH₃CN)]·(CH₃CN)₂ (1)

A solution of CuBr₂ (4.46 mg, 0.02 mmol) in acetonitrile and methanol (1 mL: 1 mL) was layered onto a solution of L (3.43 mg, 0.01 mmol) in methanol (2 mL). The solutions were left at room temperature for about one day, and light green block crystals (3.26 mg) were obtained. Yield: 51%. IR (KBr pellet cm⁻¹): 3385(w), 2970(w), 2841(w), 2140(w), 1917(w), 1546(s), 1471(m), 1309(w), 1236(m), 1166(m), 1009(m), 898(s), 805(w), 657(w), 529(s), 480(m). Elemental analysis Calcd (%) for $C_{21}H_{20}Br_2CuN_8S$: C 39.42, H 3.15, N 17.51; Found: C 39.56, H 3.38, N 17.39. The green crystals of **1** were taken out from the mother liquid, and stood in air overnight, brown crystals of Cu(L)Br₂(0.5 CH₃CN)·(0.25 CH₃CN) (**2**) were obtained. Elemental analysis Calcd (%) for $C_{18.5}H_{16.25}Br_2CuN_{6.75}S$: C 37.75, H 2.78, N 16.06; Found: C 38.22, H 2.90, N 15.65.

Preparation of [Cu(L)Br₂(CH₃OH)]·(CH₂Cl₂) (CH₃OH) (3)

A solution of CuBr_2 (4.46 mg, 0.02 mmol) in methanol (2 mL) was layered onto a solution of L (3.43 mg, 0.01 mmol) in dichloromethane (2 mL). The solutions were left at room temperature for about 7 days, and blue block crystals (5.50 mg) were obtained. Yield: 78%.

IR (KBr pellet cm⁻¹): 3374 (w), 2938 (w), 2829 (w), 2105 (w), 1912 (w), 1597 (s), 1499 (w), 1429 (s), 1312 (m), 1249 (m), 1194 (m), 1093 (m), 1013 (s), 862 (w), 809 (s), 689 (w), 583 (w), 479 (m). Elemental analysis Calcd (%) for $C_{20}H_{24}Br_2Cl_2CuN_6O_2S$: C 33.99, H 3.42, N 11.89; Found: C 33.85, H 3.50, N 11.71.

Preparation of [Cu(L)Br₂(THF)]·(CH₃OH) (4)

A solution of CuBr₂ (4.46 mg, 0.02 mmol) in methanol (2 mL) was layered onto a solution of L (3.43 mg, 0.01 mmol) in THF (2 mL). The solutions were left at room temperature for about 7 days, and green block crystals (3.74 mg) were obtained. Yield: 57%. IR (KBr pellet cm⁻¹): 3369 (w), 2901 (w), 2834 (w), 2100 (w), 1899 (w), 1581 (s), 1470 (w), 1404 (s), 1298 (m), 1177 (m), 1005 (m), 1057 (m), 874 (w), 699 (w), 583 (w), 478 (s). Elemental analysis Calcd (%) for $C_{22}H_{26}Br_2CuN_6O_2S$: C 39.92, H 3.96, N 12.70; Found: C 40.36, H 3.78, N 12.39.

Preparation of [Cu(L)Br₂(DMF)]·(C₂H₅OH) (5)

A solution of CuBr₂ (4.46 mg, 0.02 mmol) in ethanol (2 mL) was layered onto a solution of L (3.43 mg, 0.01 mmol) in DMF (2 mL). The solutions were left at room temperature for about 7 days, and green block crystals (3.04 mg) were obtained. Yield: 46%. IR (KBr pellet cm⁻¹): 3396 (w), 2988 (w), 2877 (w), 2221 (w), 1967 (w), 1506 (s), 1488 (m), 1376 (w), 1246 (m), 1190 (m), 1017 (m), 902 (s), 837 (w), 611 (w), 544 (s), 467 (m). Elemental analysis Calcd (%) for $C_{21}H_{24}Br_2CuN_7O_{1.5}S$: C 38.57, H 3.70, N 14.99; Found: C 38.90, H 3.55, N 14.52.

Powder X-ray diffraction (PXRD) patterns were recorded to check the purity of the samples of **3-5** (Figure S10). The peak positions of the simulated patterns using the single crystal data and experimental PXRD patterns are in good agreement with each other.

2. Crystallographic data

Suitable single crystals of complexes were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 100.01 K on an Agilent SuperNova CCD-based diffractometer (Cu K α radiation ($\lambda = 1.54184$ Å). The raw frame data for the complexes were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.² Corrections for incident and diffracted beam

absorption effects were applied using SADABS.³ None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by full-matrix leastsquares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions with isotropic displacement parameters set to $1.2U_{eq}$ of the attached atom. For compound **2**, the bond lengths of N7-C18, N8-C21 were restrained to be 1.118(10)-1.125(10) Å, and the C18-C19, C20-C21 bond lengths were restrained to be 1.533(10) and 1.519(10)Å. The ADPs of atoms N8, C20 and C21 same within a standard deviation of 0.005 $Å^2$, were restrained to be and The ADPs of atoms N7, C19 C18 and were restrained to be isotropy within a standard deviation of 0.002 Å². Total 37 restrains were used to model the acetonitrile molecules.

	1	2
Formula	$C_{21}H_{20}Br_2CuN_8S$	$C_{18.5}H_{16.25}Br_2CuN_{6.75}S$
Formula weight	639.87	588.55
temp(K)	100.01(10)	112(19)
crystal system	Orthorhombic	Orthorhombic
space group	P n a 21	P n a 21
<i>a</i> (Å)	8.6476(3)	8.4816(6)
<i>b</i> (Å)	15.2470(4)	15.3597(17)
<i>c</i> (Å)	20.5679(7)	19.7243(15)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
V (Å ³)	2711.89(16)	2569.6(4)
Z	4	4
ρ calc (g/cm ³)	1.567	1.521
μ (mm ⁻¹)	5.505	5.741

F (000)	1268	1158
GOF on F ²	1.082	1.066
data/restraints/parameters	3708 / 8 / 329	3490 / 37 / 310
final R indices	R1 = 0.0442	R1 = 0.0843
[I>2sigma(I)]	wR2 = 0.1269	wR2 = 0.2284

^{*a*} $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^{*b*} $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{0.5}$.

 Table S2. Crystallographic data for 3-5.

	3	4	5
Formula	$C_{20}H_{24}Br_2Cl_2CuN_6O_2S$	$C_{22}H_{26}Br_2CuN_6O_2S$	$C_{21}H_{24}Br_2CuN_7O_{1.5}S$
Formula weight	706.77	661.91	653.89
temp(K)	100.01(10) K	298(2) K	100.01(10)
crystal system	Orthorhombic	Orthorhombic	Orthorhombic
space group	P n a 21	P n a 21	P n a 21
<i>a</i> (Å)	8.7520(2)	8.8761(3)	8.7700(3)
<i>b</i> (Å)	15.3925(3)	15.2703(5)	14.9616(4)
<i>c</i> (Å)	20.4584(4)	21.1399(11)	20.7948(6)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
V (Å ³)	2756.06(10)	2865.3(2)	2728.55(13)
Ζ	4	4	4
ρ calc (g/cm ³)	1.703	1.534	1.592
μ (mm ⁻¹)	7.254	5.260	5.514

F (000)	1404	1324	1304
GOF on F ²	1.080	1.090	1.096
data/restraints/parameters	3412 / 1 / 310	4114 / 3 / 326	3364 / 4 / 318
final R indices	R1 = 0.0405	R1 = 0.0460	R1 = 0.0552
[I>2sigma(I)]	wR2 = 0.1083	wR2 = 0.1388	wR2 = 0.1563

^{*a*} $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$. ^{*b*} $wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{0.5}$.

Table S3. Selected bond angles (°) and Cu…Cu distances (Å) of importance to magnetic exchanges between Cu(II) ions. Parameters characterizing the magnetic properties of the compounds.

	1(MeCN)	2 (0.5MeCN)	3 (MeOH)	4 (THF)	5 (DMF)
∠Br1-Cu1-Br2	159.1(2)	161.3(2) 158.1(2)	158.0(2)	161.2(2)	161.2(2)
Shortest interchain Cu…Cu distances	8.61; 8.92	8.75; 8.79	8.74; 8.96	8.73; 8.93	8.60; 8.75
C (cm ³ K/mol) ^a	0.41	0.44	0.40	0.40	0.42
θ (K) ^a	0.41	-5.31	1.90	-1.56	-3.36
^a Curie–Weiss fit of data between 2 and 300 K.					

Table S4. Selected bond length (Å) and angle (°)

1					
Cu(1)-N(2)#1	2.000(6)	Cu(1)-N(1)	2.004(6)		
Br(1)-Cu(1)	2.4627(14)	Br(2)-Cu(1)	2.4784(14)		
Cu(1)-N(7)	2.290(9)				
N(2)#1-Cu(1)-N(1)	169.6(3)	N(1)-Cu(1)-N(7)	94.9(3)		
N(2)#1-Cu(1)-N(7)	95.5(3)	N(2)#1-Cu(1)-Br(1)	90.19(18)		
N(1)-Cu(1)-Br(1)	86.73(17)	N(7)-Cu(1)-Br(2)	98.1(3)		
N(1)-Cu(1)-Br(2)	91.60(17)	Br(1)-Cu(1)-Br(2)	159.07(6)		
		2			
Cu(1)-N(1)	1.997(11)	Cu(1)-N(6)#2	1.970(12)		
Cu(1)-Br(1)	2.538(4)	Br(2)-Cu(1)	2.443(3)		

Cu(1)-N(7)	2.36(3)	Cu(1)-Br(1')	2.275(4)
N(6)#2-Cu(1)-N(1)	164.9(5)	N(6)#2-Cu(1)-Br(1')	95.8(4)
N(1)-Cu(1)-Br(1')	90.3(3)	N(6)#2-Cu(1)-N(7)	91.7(9)
N(1)-Cu(1)-N(7)	103.2(9)	N(6)#2-Cu(1)-Br(2)	91.2(3)
Br(2)-Cu(1)-Br(1)	161.32(19)	N(1)-Cu(1)-Br(2)	88.2(3)
N(1)-Cu(1)-Br(1)	93.2(3)	Br(1')-Cu(1)-Br(2)	158.09(18)
		3	
Cu(1)-N(6)	1.993(5)	Cu(1)-N(1)#1	1.988(6)
Br(1)-Cu(1)	2.4650(12)	Br(2)-Cu(1)	2.4533(13)
Cu(1)-O(1)	2.209(5)		
N(1)#1-Cu(1)-N(6)	171.1(2)	N(1)#1-Cu(1)-O(1)	93.6(2)
N(6)-Cu(1)-O(1)	95.2(2)	N(1)#1-Cu(1)-Br(2)	90.44(16)
N(6)-Cu(1)-Br(2)	87.50(16)	O(1)-Cu(1)-Br(2)	105.28(14)
Br(2)-Cu(1)-Br(1)	158.03(6)	N(6)-Cu(1)-Br(1)	91.21(15)
		4	
Cu(1)-N(1)	2.006(5)	Cu(1)-N(6)#1	2.002(5)
Br(1)-Cu(1)	2.4575(13)	Br(2)-Cu(1)	2.4606(14)
Cu(1)-O(1)	2.324(6)		
N(6)#1-Cu(1)-N(1)	172.2(2)	Br(1)-Cu(1)-Br(2)	161.16(7)
O(1)-Cu(1)-Br(2)	101.94(16)	N(1)-Cu(1)-Br(2)	90.46(17)
N(6)#1-Cu(1)-Br(2)	88.88(17)	O(1)-Cu(1)-Br(1)	96.89(17)
N(1)-Cu(1)-Br(1)	87.60(16)	N(1)-Cu(1)-O(1)	94.3(2)
		5	
Cu(1)-N(6)#1	1.996(7)	Cu(1)-N(1)	2.007(7)
Br(1)-Cu(1)	2.4725(18)	Br(2)-Cu(1)	2.4679(18)
Cu(1)-O(1)	2.207(8)		
N(6)#1-Cu(1)-N(1)	168.3(3)	N(6)#1-Cu(1)-O(1)	96.1(3)
N(1)-Cu(1)-O(1)	95.3(3)	N(6)#1-Cu(1)-Br(2)	89.6(2)
N(1)-Cu(1)-Br(2)	91.2(2)	N(1)-Cu(1)-Br(1)	86.1(2)
O(1)-Cu(1)-Br(1)	98.6(4)	Br(2)-Cu(1)-Br(1)	161.19(8)

Symmetry transformations used to generate equivalent atoms:

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

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

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

4: #1 -x+1, -y+1, z+1/2; #2 -x+1, -y+1, z-1/2

5: #1 -x+1, -y, z+1/2; #2 -x+1, -y, z-1/2

Table S5. Hydrogen bonds for **1** [Å and °]

D-HA	d(D-H)	d(HA)	d(DA)	∠DHA
N(6)-H(6B)N(3)#3	0.87	2.61	3.451(8)	160.7
N(6)-H(6B)N(4)#3	0.87	2.37	3.080(8)	138.0
N(6)-H(6A)Br(2)#4	0.87	2.89	3.642(6)	145.6
C(1)-H(1)N(8)#5	0.93	2.89	3.426(18)	118.3
C(6)-H(6)N(9)#6	0.93	2.95	3.599(16)	127.9
C(15)-H(15)N(9) #7	0.93	2.61	3.490(17)	157.8

Symmetry transformations used to generate equivalent atoms: #3 x-1/2, -y+3/2, z; #4 x+1/2, -y+3/2, z; #5 -x+1, -y+1, z-1/2; #6 x+1, y, z; #7 -x+1, -y+1, z+1/2

Table S6. Hydrogen bonds for **2** [Å and °]

D-HA	d(D-H)	d(HA)	d(DA)	∠DHA
N(5)-H(5A)N(3)#3	0.89	2.47	3.300(17)	154.6
N(5)-H(5A)N(2)#3	0.89	2.59	3.16(2)	122.2
N(5)-H(5B)S(1)	0.89	2.59	3.030(14)	111.5
C(1)-H(1)N(8)#2	0.93	2.73	3.52(5)	143.1

Symmetry transformations used to generate equivalent atoms: #3 x-1/2, -y+3/2, z

D-HA	d(D-H)	d(HA)	d(DA)	∠DHA
N(5)-H(5B)N(2)#3	0.93	2.63	3.507(8)	158.5
N(5)-H(5B)N(3)#3	0.93	2.28	3.124(8	151.5

Table S7.Hydrogen bonds for 3 [Å and °]

N(5)-H(5A)Br(2)#4	0.95	3.04	3.869(6)	146.4
O(1)-H(1A)O(2)#1	0.93	1.82	2.721(8)	161.2
O(2)-H(2)N(3)#2	0.82	2.67	3.329(8)	138.2
O(2)-H(2)N(2)#2	0.82	2.03	2.839(8)	168.

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+2, z+1/2

#2 -x+1, -y+2, z-1/2 #3 x+1/2, -y+3/2, z #4 -x+1/2, y-1/2, z-1/2

5 6				
D-HA	d(D-H)	d(HA)	d(DA)	∠DHA
N(5)-H(5B)N(2)#3	0.87	2.67	3.529(8)	168.0
N(5)-H(5B)N(3)#3	0.87	2.42	3.128(8)	138.8
N(5)-H(5A)S(1)	0.87	2.57	3.050(6)	115.4
C(6)-H(6)O(1")	0.93	2.59	3.275(19)	131.2
C(15)-H(15)O(1")#2	0.93	2.46	3.363(2)	164.5

Table S8. Hydrogen bonds for 4 [Å and °]

Symmetry transformations used to generate equivalent atoms: #2 -x+1, -y+1, z-1/2; #3 x+1/2, -y+3/2, z.

Table S9.Hydrogen bonds for 5 [Å and °]

D-HA	d(D-H)	d(HA)	d(DA)	∠DHA
N(5)-H(5B)N(3)#4	0.88	2.36	3.095(11	141.1
)	
N(5)-H(5B)N(2)#4	0.88	2.68	3.500(11	154.8
)	
N(5)-H(5A)Br(2)#3	0.88	2.85	3.665(8)	155.1
O(2)-H(2)Br(1)	0.82	2.66	3.47(2)	169.2

Symmetry transformations used to generate equivalent atoms: #3 x-1/2, -y+1/2, z #4 x+1/2, -y+1/2, z



Figure S1. Simulated (blue) and experimental (black) powder X-ray diffraction (PXRD) patterns of polymers 1 and 2 and recovered 1'.



Figure S2. Top: coordination environment around Cu(II) center; Bottom: (left) twodimensional network in **1**, with CH₃CN guest solvent molecules located in the cavity; (middle) two adjacent helical chains possessing opposite chirality; (right) π - π interactions between the triazole and quinoline rings and quinoline and quinoline rings on adjacent chains.



Figure S3. Top: coordination environment around Cu(II) center; Bottom: (left) twodimensional network in **2**, with CH₃CN guest solvent molecules located in the channel; (middle) helical chains possessing opposite chirality extending along *b* axis; (right) π - π interactions between the triazole and quinoline rings on adjacent chains.



Scheme S1. Possible mechanism for single-crystal-to-single-crystal transformation from 1 to 2.



Figure S4. Presentation of the π - π interactions (purple dashed lines) between the triazole and quinoline rings, quinoline and quinoline rings, and pyridine and pyridine rings, as well as the interchain N–H···N and N–H···Br hydrogen-bonding interactions and the non-classical C–H···N interactions between framework and guest molecules (orange dashed lines) in **1**.



Figure S5. Presentation of the π - π interactions (purple dashed lines) between the triazole and quinoline rings, quinoline and quinoline rings, and pyridine and pyridine rings, as well as the interchain N–H···N, the intrachain N–H···S hydrogen-bonding interactions, and the non-classic C–H···N interactions between framework and guest molecules (orange dashed lines) in **2**.



Figure S6. TGA of polymers 1 and 2.



Figure S7. Top: coordination environment around Cu(II) center; Below: presentation of the π - π interactions (purple dashed lines) between the triazole and quinoline rings, quinoline and quinoline rings, and pyridine and pyridine rings, as well as the interchain N–H…N and N–H…Br hydrogen-bonding interactions, and the O–H…N and O–H…O interactions between framework and guest molecules (orange dashed lines) in complex 3.



Figure S8. Top: coordination environment around Cu(II) center; Below: presentation of the π - π interactions (purple dashed lines) between the triazole and quinoline rings, quinoline and quinoline rings, and pyridine and pyridine rings, as well as the interchain N–H…N and intrachain N–H…S hydrogen-bonding interactions, and the C–H…O interactions between framework and guest molecules (orange dashed lines) in complex 4.



Figure S9. Top: coordination environment around Cu(II) center; Below: presentation of the π - π interactions (purple dashed lines) between the triazole and quinoline rings, quinoline and quinoline rings, and pyridine and pyridine rings, as well as the interchain N-H…N and N-H…Br hydrogen-bonding interactions, and the O-H…Br interactions between framework and guest molecules (orange dashed lines) in complex 5.



Figure S10. Simulated (blue) and experimental (black) powder X-ray diffraction (PXRD) patterns of polymers **3-5**.





Figure S11. TGA curves of 3-5. The measured and calculated weight losses are 16.1 and 21.1% (for 3), 15.1 and 15.7% (for 4), 16.8 and 18.2% (for 5), respectively.

Reference

1. J. R. Reid, N.D. Heindel, J. Heterocyclic. Chem. 1976, 13, 925.

2. SMART Version 5.625 and SAINT+ Version 6.02a. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1998.

3. G. M. ldrick, SHELXTL Version 5.1; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1997.