Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information for

Reversible visual thermochromic coordination polymers via single-crystal-to-single-crystal transformation

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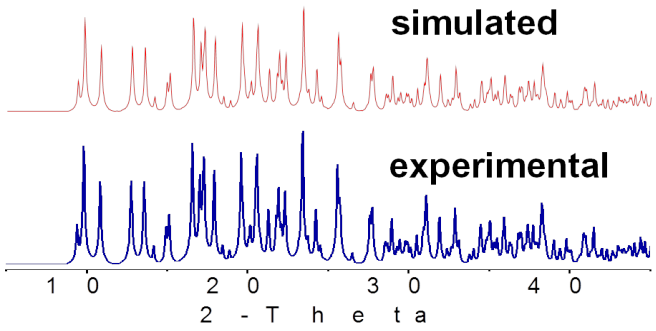
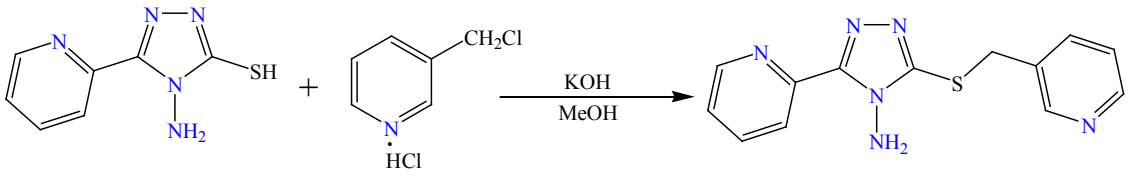


Fig. S1 XRPD pattern of **1.**

Experimental Section. Commercially available reagents were used as received without further purification. 5-(2-pyridyl)-3-mercapto-4-amino-1, 2, 4-triazole (A) was prepared According to method of 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. ^{1}H NMR data were collected using an AM-300 spectrometer. Chemical shifts are reported in δ relative to TMS. The UV-vis diffuse reflectance was performed on SHIMADZU UV-2550 UV-vis spectrophotometer.

Synthesis of L.



A L

A solution of **A** (2.28g， 12mmol), 3-(Chloromethyl)pyridine Hydrochloride (2.16g, 13.2mmol), KOH (1.6g, 15.6mmol) in 30mL MeOH, was stirred for 24 hours. The obtained sample was purified by column to generate colorless crystalline solids 2.07 g (Yield, 60.8 %). ^{1}H NMR (300MHz, $CDCl_3$, 25°C TMS, ppm): δ 8.65(s, 1H, -C_5H_4N), 8.58(d, 1H, -C_5H_4N), 8.47(t, 1H, -C_5H_4N), 8.22 (d, 1H, -C_5H_4N), 7.84~7.82(m, 2H, -C_5H_4N), 7.35~7.33(m, 1H, -C_5H_4N), 7.39(s, 1H, -C_5H_4N), 7.29~7.20(m, 1H, -C_5H_4N), 6.20(s, 2H, -NH_2), 4.48(s, 2H, -CH_2-). IR (KBr pellet cm^{-1}): 3442(vs), 1638(s), 1591(s), 1571(s), 1465(s), 1424(vs) , 1252(m), 1194(w), 1101(w), 1013(m), 957(m), 811(m), 789(m), 739(w), 712(w), 681(w), 628(w).. Elemental analysis Calcd (%) for $C_{13}H_{12}N_6S$: C 54.92, H 4.23, N 29.58; Found: C 54.87, H 4.18, N 29.53.

Single-Crystal Structure Determination. The variable temperature X-ray diffraction data of **1-4** were measured on Agilent Gemini E diffractometer (Mo Kα radiation, λ = 0.71073 Å). The raw frame data for **1** - **4** 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.[2] The crystals showed no evidence of crystal decay during data collection. The structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least squares technique, using the SHELXTL software package.[3] The asymmetric unit contains the Cu atom, one coordinated $C_{13}H_{12}N_6S$ ligand, a uncoordinated $SO_3CF_3^-$ of crystallization. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to refined atoms were placed in geometrically idealized positions and refined using a riding model. Crystal data, data collection parameters, and refinement statistics for **1, 2, 3** and **4** are listed in Tables 1.

Table S1. Crystal data collection and structure refinement for compounds **1-4.**

compound	**1**	**2**	**3**	**4**
empirical formula	$C_{28}H_{24}CuF_6N_{12}O_6S_4$	$C_{28}H_{24}CuF_6N_{12}O_6S_4$	$C_{28}H_{24}CuF_6N_{12}O_6S_4$	$C_{28}H_{24}CuF_6N_{12}O_6S_4$
formula weight	930.37	930.37	930.37	930.37
temp (K)	298(2)	323(2)	353(2)	298(2)
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	*P2(1)/n*	*P2(1)/n*	*P2(1)/n*	*P2(1)/n*
a (Å)	9.2150(3)	9.2224(7)	9.2249(9)	9.2121(8)
b (Å)	18.8491(5)	18.8786(13)	18.8564(13)	18.8386(13)
c (Å)	10.4290(3)	10.4661(8)	10.4413(11)	10.4187
α(deg)	90	90	90	90
β(deg)	100.392(3)	100.366(7)	100.292(10)	100.408(9)

γ(deg)	90	90	90	90
V (Å^3)	1781.75(10)	1792.5(2)	1787.0(3)	1778.3(3)
Z	2	2	2	2
ρcalc (g/cm^3)	1.734	1.724	1.729	1.737
F(000)	942	942	942	942
data/restraints/params	3318 / 1 / 259	3348 / 0 / 259	3332 / 0 / 259	3312 / 0 / 259
GOF on F^2	1.048	1.081	1.079	1.060
final R indices [I >	R1 = 0.0333	R1 = 0.0434	R1 = 0.0444	R1 = 0.0488
2sigma(I)]	wR2 = 0.0725	wR2 = 0.0823	wR2 = 0.0874	wR2 = 0.0847

Table S2. Interatomic Distances (Å) and Bond Angles (°) with esds () for **1**.

Cu(1)-N(3)=1.9754(18)	Cu(1)-N(3)#1=1.9754(18)	Cu(1)-N(2)#2=2.126(2)
Cu(1)-N(2)#3=2.126(2)	Cu(1)-N(1)#1=2.390(2)	Cu(1)-N(1)=2.390(2)
N(2)-Cu(1)#4=2.126(2)		

N(3)-Cu(1)-N(3)#1 = 180.00(7)	N(3)-Cu(1)-N(2)#2 = 90.45(8)
N(3)#1-Cu(1)-N(2)#2 = 89.55(8)	N(3)-Cu(1)-N(2)#3 = 89.55(8)
N(3)#1-Cu(1)-N(2)#3 = 90.45(8)	N(2)#2-Cu(1)-N(2)#3 = 180.00(9)
N(3)-Cu(1)-N(1)#1 = 105.09(7)	N(3)#1-Cu(1)-N(1)#1 = 74.91(7)
N(2)#2-Cu(1)-N(1)#1 = 87.29(7)	N(2)#3-Cu(1)-N(1)#1 = 92.71(7)
N(3)-Cu(1)-N(1) = 74.91(7)	N(3)#1-Cu(1)-N(1) = 105.09(7)
N(2)#2-Cu(1)-N(1) = 92.71(7)	N(2)#3-Cu(1)-N(1) = 87.29(7)
N(1)#1-Cu(1)-N(1) = 180.0	C(1)-N(1)-C(5) = 117.6(2)
C(1)-N(1)-Cu(1) = 131.84(19)	C(5)-N(1)-Cu(1) = 110.19(15)
C(12)-N(2)-C(13) = 117.7(2)	C(12)-N(2)-Cu(1)#4 = 119.20(16)
C(13)-N(2)-Cu(1)#4 = 123.11(17)	

Symmetry transformations used to generate equivalent atoms:

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

Table S3. Interatomic Distances (Å) and Bond Angles (°) with esds () for **2**.

Cu(1)-N(3) = 1.977(2)	Cu(1)-N(3)#1 = 1.977(2)	Cu(1)-N(2)#2 = 2.132(3)
Cu(1)-N(2)#3 = 2.132(3)	Cu(1)-N(1) = 2.380(3)	Cu(1)-N(1)#1 = 2.380(3)
N(2)-Cu(1)#4 = 2.132(3)		

N(3)-Cu(1)-N(3)#1 = 180.00(14)	N(3)-Cu(1)-N(2)#2 = 90.51(10)
N(3)#1-Cu(1)-N(2)#2 = 89.49(10)	N(3)-Cu(1)-N(2)#3 = 89.49(10)
N(3)#1-Cu(1)-N(2)#3 = 90.51(10)	N(2)#2-Cu(1)-N(2)#3 = 180.00(11)
N(3)-Cu(1)-N(1) = 74.98(10)	N(3)#1-Cu(1)-N(1)=105.02(10)
N(2)#2-Cu(1)-N(1)=92.72(10)	N(2)#3-Cu(1)-N(1)=87.28(10)
N(3)-Cu(1)-N(1)#1=105.02(10)	N(3)#1-Cu(1)-N(1)#1=74.98(10)
N(2)#2-Cu(1)-N(1)#1=87.28(10)	N(2)#3-Cu(1)-N(1)#1=92.72(10)
N(1)-Cu(1)-N(1)#1=180.0	

Symmetry transformations used to generate equivalent atoms:

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

Table S4. Interatomic Distances (Å) and Bond Angles (°) with esds () for **3**.

Cu(1)-N(3) = 1.970(2)	Cu(1)-N(3)#1 = 1.970(2)	Cu(1)-N(2)#2 = 2.140(3)
Cu(1)-N(2)#3 = 2.140(3)	Cu(1)-N(1)#1 = 2.372(3)	Cu(1)-N(1) = 2.372(3)
N(2)-Cu(1)#4 = 2.140(3)		

N(3)-Cu(1)-N(3)#1 = 180.00(10)	N(3)-Cu(1)-N(2)#2 = 89.36(10)
N(3)#1-Cu(1)-N(2)#2 = 90.64(10)	N(3)-Cu(1)-N(2)#3 = 90.64(10)
N(3)#1-Cu(1)-N(2)#3 = 89.36(10)	N(2)#2-Cu(1)-N(2)#3 = 180.0
N(3)-Cu(1)-N(1)#1 = 104.87(10)	N(3)#1-Cu(1)-N(1)#1 = 75.13(10)
N(2)#2-Cu(1)-N(1)#1 = 92.95(10)	N(2)#3-Cu(1)-N(1)#1 = 87.05(10)
N(3)-Cu(1)-N(1) = 75.13(10)	N(3)#1-Cu(1)-N(1) = 104.87(10)
N(2)#2-Cu(1)-N(1) = 87.05(10)	N(2)#3-Cu(1)-N(1) = 92.95(10)
N(1)#1-Cu(1)-N(1) = 180.00(10)	

Symmetry transformations used to generate equivalent atoms:

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

Table S5. Interatomic Distances (Å) and Bond Angles (°) with esds () for **4**.

Cu(1)-N(3)#1=1.972(3)	Cu(1)-N(3)=1.972(3)	Cu(1)-N(2)#2=2.121(3)
Cu(1)-N(2)#3=2.121(3)	Cu(1)-N(1)=2.387(3)	Cu(1)-N(1)#1=2.387(3)
N(2)-Cu(1)#4=2.121(3)		

N(3)#1-Cu(1)-N(3) = 180.00(12)	N(3)#1-Cu(1)-N(2)#2 = 89.52(12)
N(3)-Cu(1)-N(2)#2 = 90.48(12)	N(3)#1-Cu(1)-N(2)#3 = 90.48(12)
N(3)-Cu(1)-N(2)#3 = 89.52(12)	N(2)#2-Cu(1)-N(2)#3 = 180.00(12)
N(3)#1-Cu(1)-N(1) = 105.19(11)	N(3)-Cu(1)-N(1) = 74.81(11)
N(2)#2-Cu(1)-N(1) = 92.77(11)	N(2)#3-Cu(1)-N(1) = 87.23(11)
N(3)#1-Cu(1)-N(1)#1 = 74.81(11)	N(3)-Cu(1)-N(1)#1 = 105.19(11)
N(2)#2-Cu(1)-N(1)#1 = 87.23(11)	N(2)#3-Cu(1)-N(1)#1 = 92.77(11)
N(1)-Cu(1)-N(1)#1 = 180.000(1)	

Symmetry transformations used to generate equivalent atoms:

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

Reference

(1) Reid, J.-R.; Heindel, N.D. *J. Heterocyclic. Chem.* **1976**, *13*, 925.

(2) Bruker Analytical X-ray Systems, Inc.: Madison, WI, **1998**.

(3) Sheldrick, G. M. SHELXTL Version 5.12; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, **1997**.