Supporting Information

Copper(I)-Iodide Based Coordination Polymers: Bifunctional Properties Related to Thermochromism and PMMA-Doped Polymer Film Materials

Yang Song[a], Ruiqing Fan[a*], Ping Wang[a], Xinming Wang[a], Song Gao[a], Xi Du[a], Yulin Yang[a*] and Tianzhu Luan[b]

[a] Department of Chemistry, Harbin Institute of Technology, Harbin 150001, P. R. of China

[b]The First Affiliated Hospital of Harbin Medical University, Harbin 150001, P. R. of China

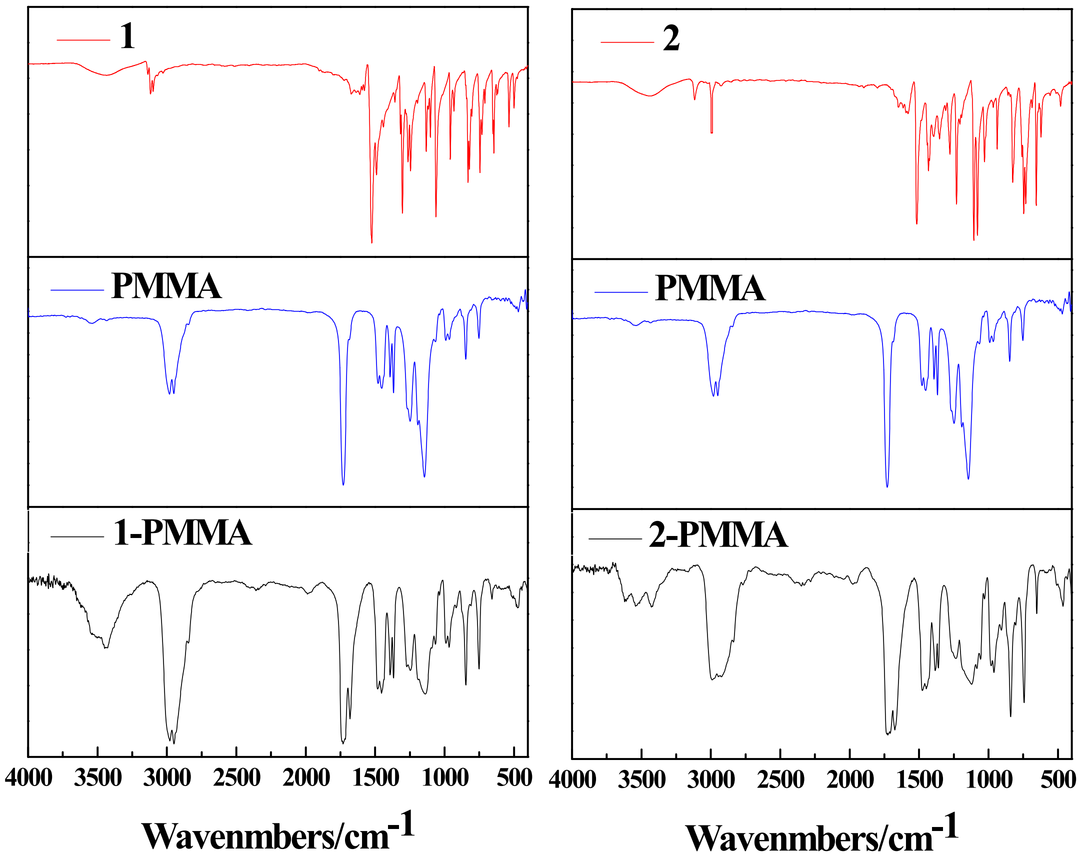

Fig.S1 The IR spectra of pure PMMA, coordination polymers **1**, **2** and **1**-PMMA, **2**-PMMA.

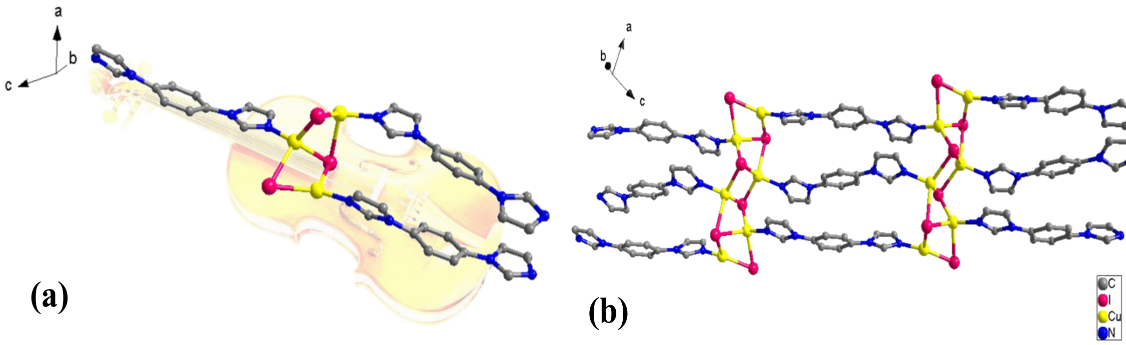

Fig.S2 (a) The structural unit of **1** with labeling scheme and 50% thermal ellipsoids (hydrogen atoms are omitted for clarity). (b) The 1D chain structure in the coordination polymer **1**.

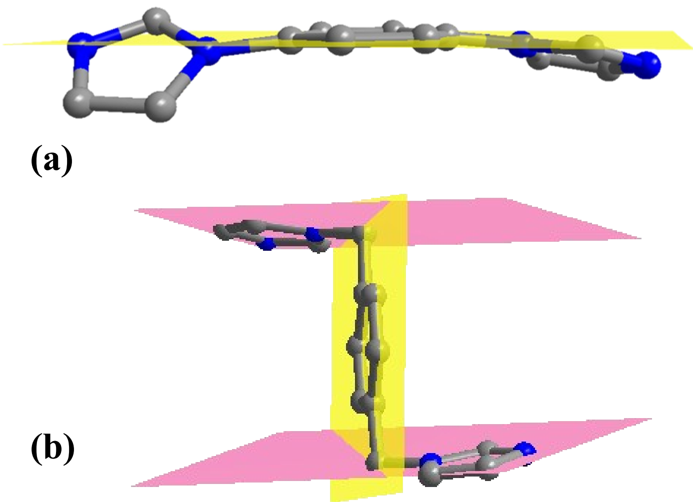

Fig.S3 The coplanarity of ligand bib and the twist of ligand bix.

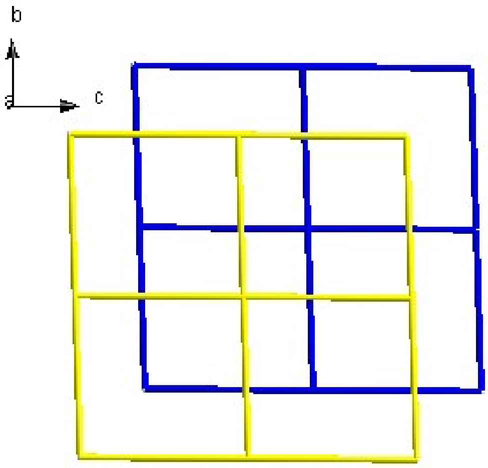

Fig.S4 The independent two-fold non-interpenetrating frameworks with **sql** network in **2**.

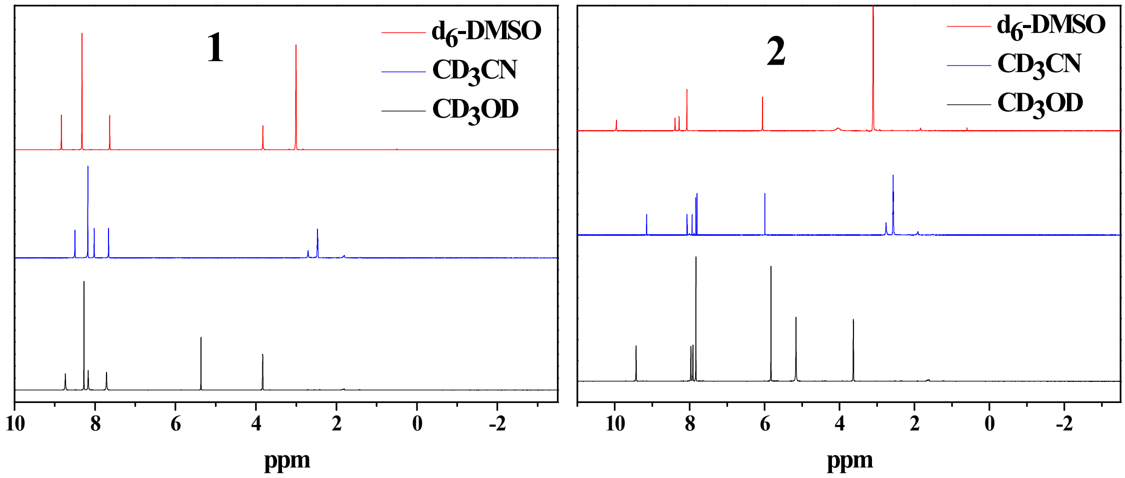

Fig.S5 The ^{1}H NMR spectra of **1** and **2**.

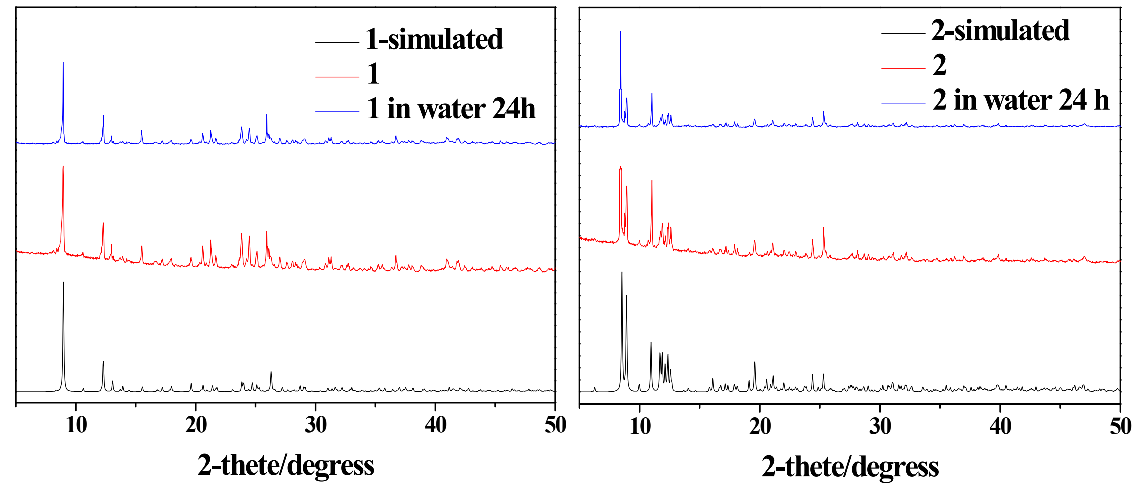

Fig.S6 The PXRD patterns of coordination polymers **1** and **2** with the relevant simulated patterns, and **1** and **2** samples soaked in water for 24 h.

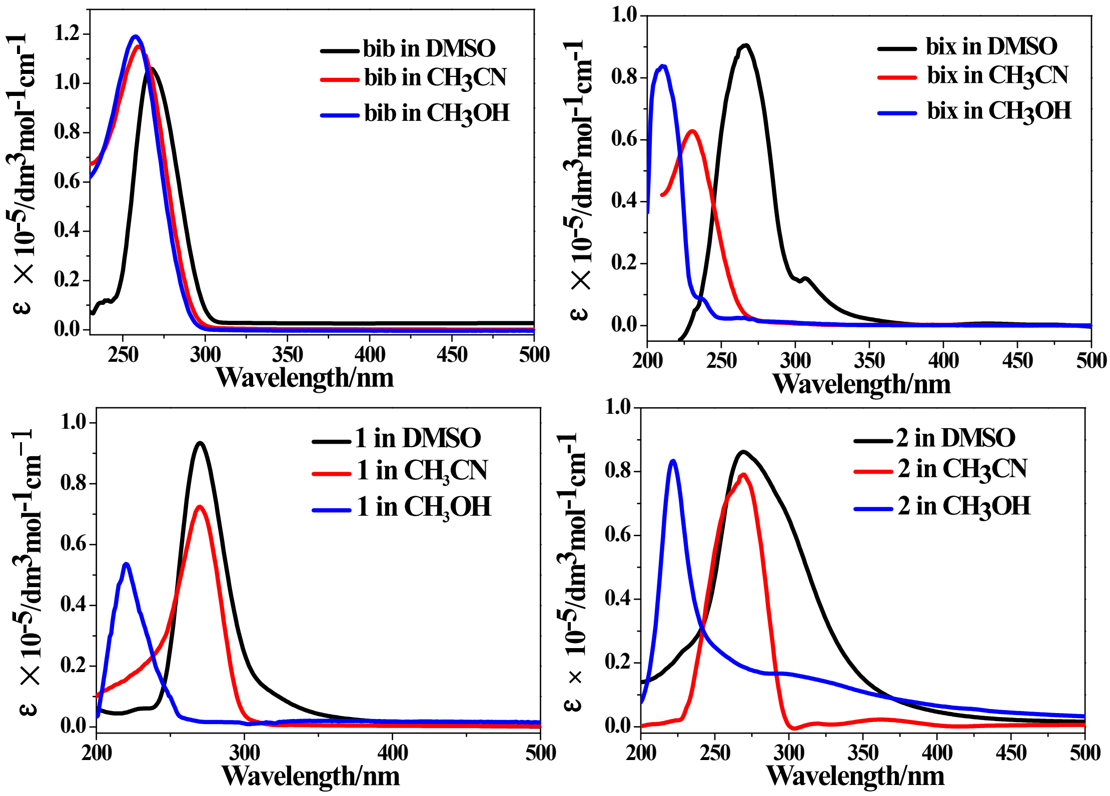

Fig.S7 UV absorption spectra of bib, bix and coordination polymers **1** and **2**.

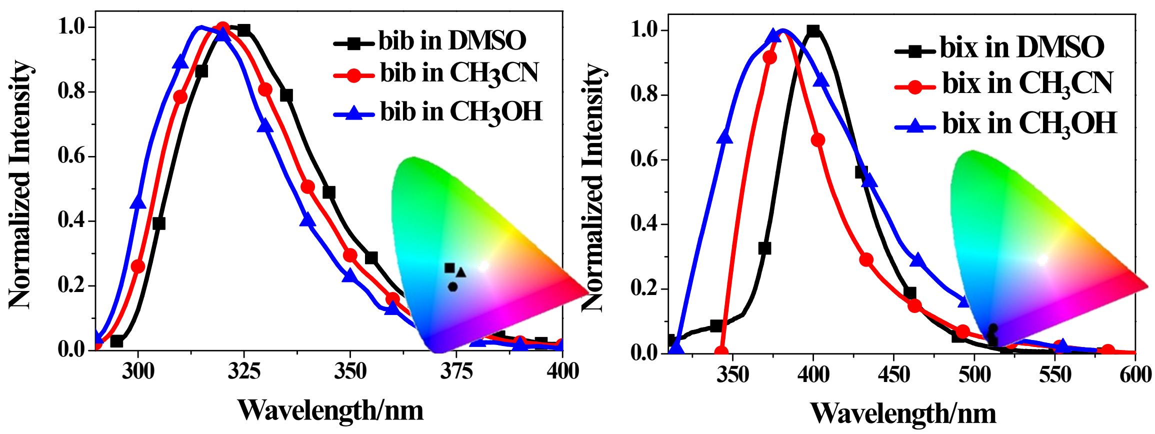

Fig.S8 Normalized emission spectra of ligands bib and bix in DMSO, CH_3CN and CH_3OH solutions (concentration: (M) ≈ 10^{-5} M) at 298 K and the corresponding color coordinate diagram of emission.

Table S1 The summary of the luminescent properties of Cu_4I_4-based luminescent materials.

No.	Cite	Complex	Excitation and emission		Luminescent character
1	*Chem. Mater.* 2008, **20**, 7010–7016	$[Cu_4I_4(PPh_2(CH_2)_2Si(OCH_2CH_3)_3)_4]$ (C1) $[Cu_4I_4\text{-}(PPh_2(CH_2)_2CH_3)_4]$ (C2)	295 K 87 K	λ_{ex} = 300 nm λ_{em} = 585 nm(C1) λ_{em} = 553 nm(C2) λ_{ex} = 300 nm λ_{em} = 312 nm (C1) λ_{em} =425 and 572 nm (C2)	a) Bright yellow luminescence at room temperature and blue (C1) and purple (C2) luminescence at 77 K. b) Dual emission. c) Large blue-shifts of 273 and 128 nm for C1 and C2.
2	*Angew. Chem. Int. Ed.* 2008, **47**, 685 –688	$[Cu_4I_4L_2]_n$ [L = 2-(cyclohexylthio)-1- thiomor pholinoethanone]	298 K 77 K	λ_{ex} = 350 nm λ_{em} = 538 nm λ_{ex} = 350 nm λ_{em} = 599 nm	a) Orange luminescence at room temperature and red luminescence at 77 K. b) Large red-shifts of 61 nm.
3	*J. Am. Chem. Soc.* 2010, **132**, 10967–10969	$[Cu_4I_4(PPh_2(CH_2CH{=}CH_2))_4]$	275 K 8 K	λ_{ex} = 360 nm λ_{em} = 530 nm λ_{ex} = 360 nm λ_{em} = 440 nm	a) Pale green luminescence at 295 K and blue luminescence at 77 K. b) Large blue-shift of 90 nm.
4	*Chem. Eur. J.*, 2010, **16**, 1553-1559	$[Cu_4I_4\text{-}(DABCO)_2]$(DABCO=1,4-diazabicyclo [2.2.2]octane) with two different crystalline forms, I and II.	295 K 77 K	λ_{ex} = 349 nm λ_{em} = 580 nm (I) λ_{em} =556 nm (II) λ_{ex} = 339 nm λ_{em} = 590 nm (I) λ_{em} =578 nm (II)	a) Emission colour from yellow at 295 K to deep orange at 77 K. b) Red-shifts of 10 and 22 nm for I and II.

5	*Chem. Commun.,* 2011, **47**, 12441–12443	$[Cu_4I_4(NH_3)Cu_3L_3]_n$ [L=3-(4-pyridyl)-5-(*p*-tolyl) pyrazolate]	293 K λ_{ex} = 365 nm λ_{em} = 530 and 700 nm 77 K λ_{ex} = 365 nm λ_{em} = 530nm	a) The luminescence changes correspondingly from yellow to brighter green from 293 K to 77 K. b) Dual emission
6	*Chem. Commun.*, 2013, **49**, 6152-6154	$[Cu_4I_4(dmimpr)_2]_n$ [dmimpr = 1,3-di(2-meth yl-imidazol-1-yl)- propane]	298 K λ_{ex} = 360 nm λ_{em} = 555nm 220 K λ_{ex} = 360 nm λ_{em} = 565nm 183 K λ_{ex} = 360 nm λ_{em} = 572nm 77 K λ_{ex} = 360 nm λ_{em} = 596 nm	a) Bright yellow luminescence at room temperature and orange-red luminescence at 77 K. b) Large red-shifts of 41 nm.
7	*Chem. Sci.*, 2013, **4**, 1484-1489	$[(Cu^I{}_4I_4)_3(Cu^I{}_6)_2(3\text{-ptt})_{12}]_n \cdot 24nDEF \cdot 12nH_2O$	RT λ_{ex} = 275 and 370 nm λ_{em} = 780 and 795nm 77 K λ_{ex} = 323 and 365 nm λ_{em} = 590, 834/590, 834 nm 10 K λ_{ex} = 323 and 365 nm λ_{em} = 594, 841/592, 853 nm	a) Emission with both thermochromic and NIR luminescence b) Dual emission c) Large red-shift of about 50 nm.
8	*Chem. Eur. J.* 2013, **19**, 15831 – 15835	$[Cu_4I_4(PPh_2(C_6H_4)CH_2OH)_4]$	290 K λ_{ex} = 300 nm λ_{em} = 535 nm 8 K λ_{ex} = 300 nm λ_{em} = 425 nm	a) Green emission at the room-temperature becomes blue emission in liquid nitrogen. b) Large blue-shift of 110 nm.

9	*Cryst. Growth Des*. 2014, **14**, 5373−5387	[{$Cu_4(\mu_3\text{-}I)_4$}(μ-L_8)$_2$]$_n$ [L8=bis(5-tert-butyl-2-methylphenylthio)-Methane]	298 K λ_{ex} = 341 nm λ_{em} = 587 nm 77 K λ_{ex} = 334 nm λ_{em} = 417 and 638 nm	a) Bright yellow luminescence at room temperature and red luminescence at 77 K. b) Large shift of 51 nm. c) Dual emission.
10	*CrystEngComm,* 2014 , **16**, 1927–1933	[Cu_4I_4(bpmp)$_2$]$_n$ (1) [bpmp=1,4-bis(pyridin-4-ylmethyl)piperazine]	298 K λ_{ex} = 365 nm λ_{em} = 585 nm 77 K λ_{ex} = 365 nm λ_{em} = 615 nm	a) Bright yellow luminescence at room temperature and orange-red luminescence at 77 K. b) A red shift of 30 nm
11	*Chem. Eur. J.* 2015, **21**, 1439 – 1443	[$Cu_4I_4L_2$(MeCN)$_2$]$_n$ (1) [$Cu_4I_4L_2$]$_n$ (2) {[$Cu_4I_4L_2$]·MeOH}$_n$ (3) [L=2-(tert-butylthio)-N-(pyridin-3-yl)-Acetamide]	298 K λ_{ex} = 350 nm λ_{em} = 460 nm (1) λ_{em} = 590 nm (2) λ_{em} = 530 nm (3) 303 K λ_{ex} = 350 nm λ_{em} =590 nm (1) λ_{em} = 590 nm (2) λ_{em} = 595 nm (3)	a) Blue, orange and yellow emission at room temperature for 1, 2 and 3, respectively, and orange emission at 303 K. b) Large red-shfits of 130 and 65 nm for 1 and 3.

Table S2 Selected bond lengths (Å) and bond angles (°) for coordination polymers **1** and **2**.

1			
I(1)-Cu(1)	2.515(1)	N(3)-Cu(2)-I(2)	107.8(1)
I(1)-Cu(2)	2.690(8)	N(3)-Cu(2)-I(1)	100.2(1)
I(2)-Cu(1)	2.706(2)	I(2)-Cu(2)-I(1)	108.2(0)
I(2)-Cu(2)	2.667(2)	N(3)-Cu(2)-I(3)	129.6(1)
I(2)-Cu(3)	2.782(1)	I(2)-Cu(2)-I(3)	108.7(3)
I(3)-Cu(2)	2.723(4)	I(1)-Cu(2)-I(3)	100.2(0)
I(3)-Cu(3)	2.638(1)	N(5)-Cu(3)-I(3)#2	107.6(1)
I(3)-Cu(3)#2	2.637(0)	N(5)-Cu(3)-I(3)	113.3(1)
Cu(2)-N(3)	2.001(4)	I(3)#2-Cu(3)-I(3)	116.2(3)
Cu(3)-N(5)	2.004(4)	N(5)-Cu(3)-I(2)	97.4(1)
Cu(3)-I(3)#2	2.637(2)	I(3)#2-Cu(3)-I(2)	113.2(3)
Cu(3)-Cu(3)#2	2.788(2)	I(3)-Cu(3)-I(2)	107.8(3)
Cu(1)-N(1)	1.959(4)	N(5)-Cu(3)-Cu(3)#2	131.3(1)
		N(1)-Cu(1)-I(1)	138.3(1)
		N(1)-Cu(1)-I(2)	107.7(1)
		I(1)-Cu(1)-I(2)	112.9(3)
2			
Cu(1)-N(1)	2.003(4)	N(1)-Cu(1)-I(3)	106.5(1)
Cu(1)-I(3)	2.644(1)	N(1)-Cu(1)-I(1)	106.3(1)
Cu(1)-Cu(4)	2.654(3)	N(1)-Cu(1)-I(2)	100.7(1)
Cu(1)-I(1)	2.684(2)	I(3)-Cu(1)-I(2)	113.0(3)
Cu(1)-Cu(3)	2.690(1)	I(1)-Cu(1)-I(2)	111.4(3)
Cu(1)-Cu(2)	2.702(1)	N(4)#1-Cu(2)-I(2)	108.2(1)
Cu(1)-I(2)	2.739(1)	N(4)#1-Cu(2)-I(4)	106.9(1)
Cu(2)-N(4)#1	2.006(4)	I(2)-Cu(2)-I(4)	116.5(3)
Cu(2)-Cu(4)	2.650(1)	N(4)#1-Cu(2)-I(3)	101.4(1)
Cu(2)-Cu(3)	2.656(1)	I(2)-Cu(2)-I(3)	110.7(3)
Cu(2)-I(2)	2.672(1)	I(4)-Cu(2)-I(3)	111.9(3)
Cu(2)-I(4)	2.702(0)	N(5)-Cu(3)-I(1)	110.5(1)
Cu(2)-I(3)	2.785(2)	N(5)-Cu(3)-I(2)	102.4(1)
Cu(3)-N(5)	2.005(4)	I(1)-Cu(3)-I(2)	112.4(3)
Cu(3)-I(1)	2.671(0)	N(5)-Cu(3)-I(4)	103.3(1)
Cu(3)-Cu(4)	2.719(1)	I(1)-Cu(3)-I(4)	113.9(3)
Cu(3)-I(2)	2.721(1)	I(2)-Cu(3)-I(4)	113.4(3)
Cu(3)-I(4)	2.747(1)	N(8)#2-Cu(4)-I(4)	108.7(1)
Cu(4)-N(8)#2	2.007(4)	I(3)-Cu(4)-I(4)	117.0(3)
Cu(4)-I(3)	2.665(1)	N(8)#2-Cu(4)-I(1)	99.1(1)
Cu(4)-I(4)	2.666(1)	I(3)-Cu(4)-I(1)	111.3(3)
Cu(4)-I(1)	2.843(0)	I(4)-Cu(4)-I(1)	111.0(3)

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