Supporting Information

Fine-tuning synthesis of a novel Cu^{I}/Cu^{II} mixed-valence coordination polymer

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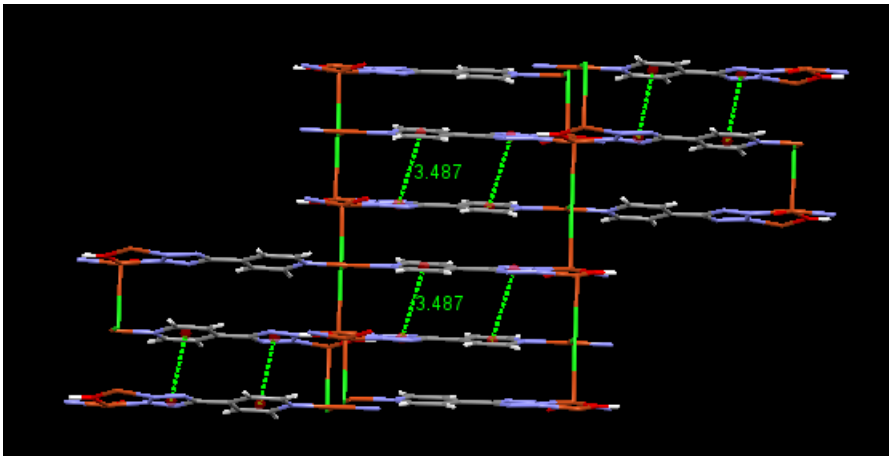
Content

(a)



(b)

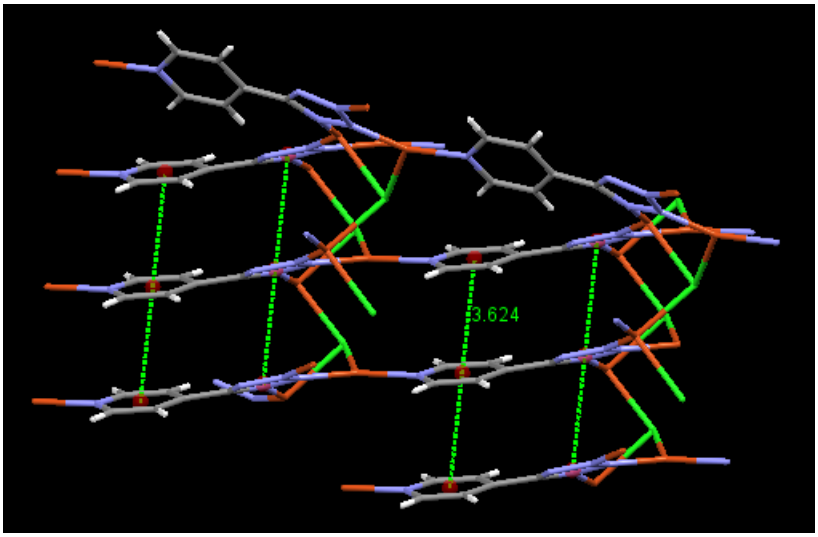


Fig. S1 Interlayer π–π stacking interactions at centroid-to-centroid distances of 3.487 Å in **1** (a), and 3.624 Å in **2** (b).

(a) (b)

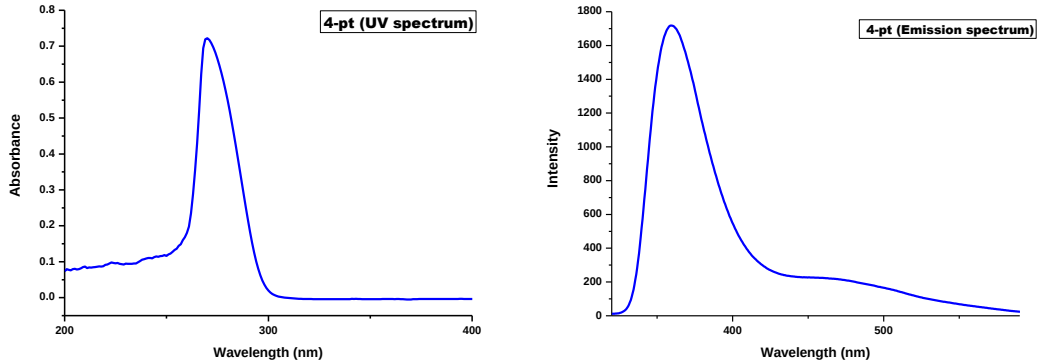


Fig. S2 (a) UV–visible absorption spectrum and (b) emission spectrum (excitation wavelength is 300 nm) of 4-H-ptz.

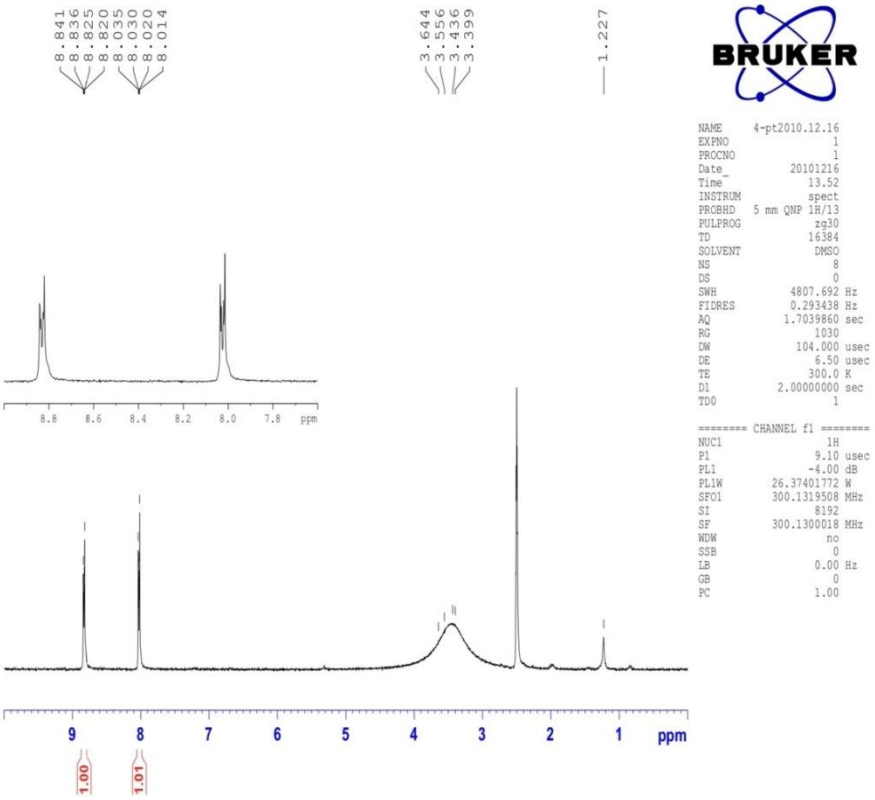


Fig. S3 NMR spectrum of of 4-H-ptz.

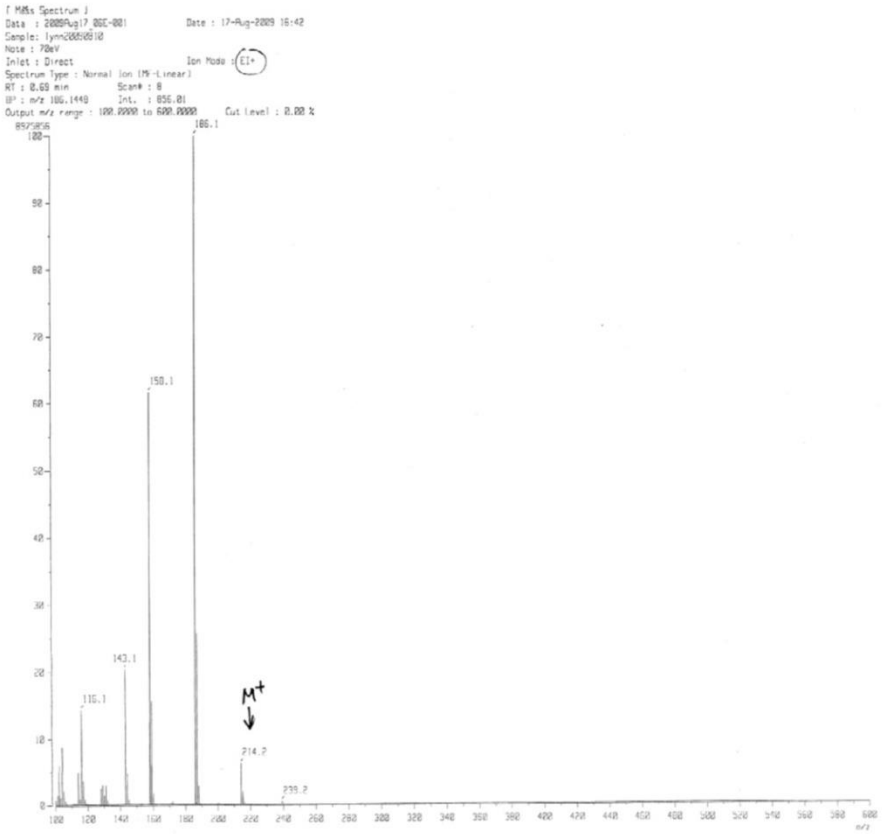


Fig. S4 Mass spectrum of 4-H-ptz.

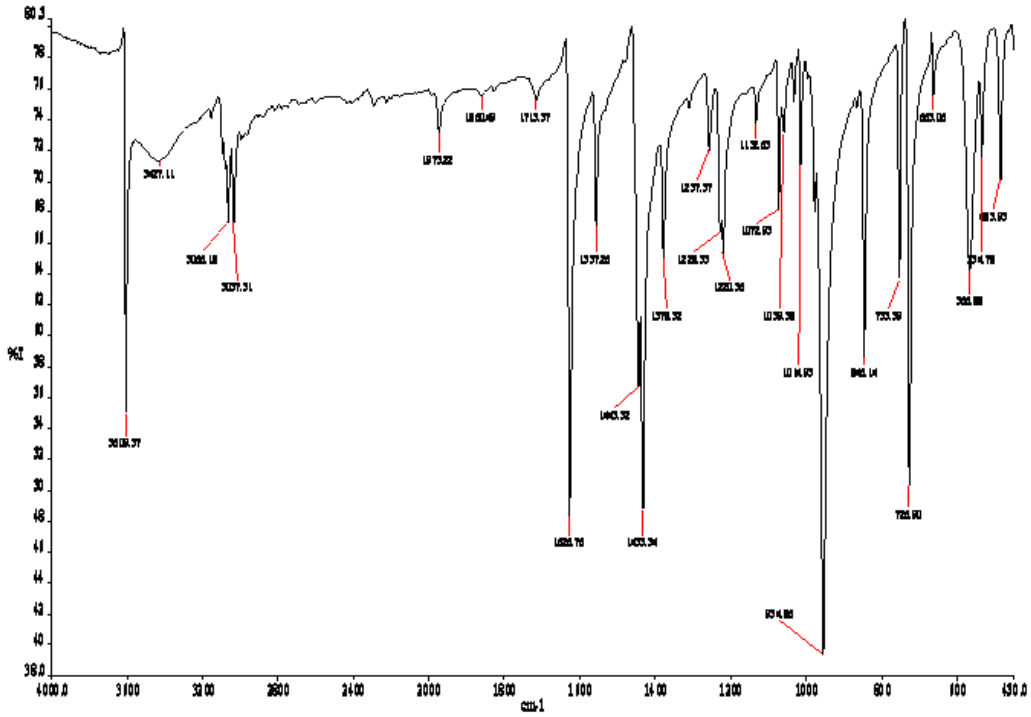


Fig. S5 IR spectrum of **1**.

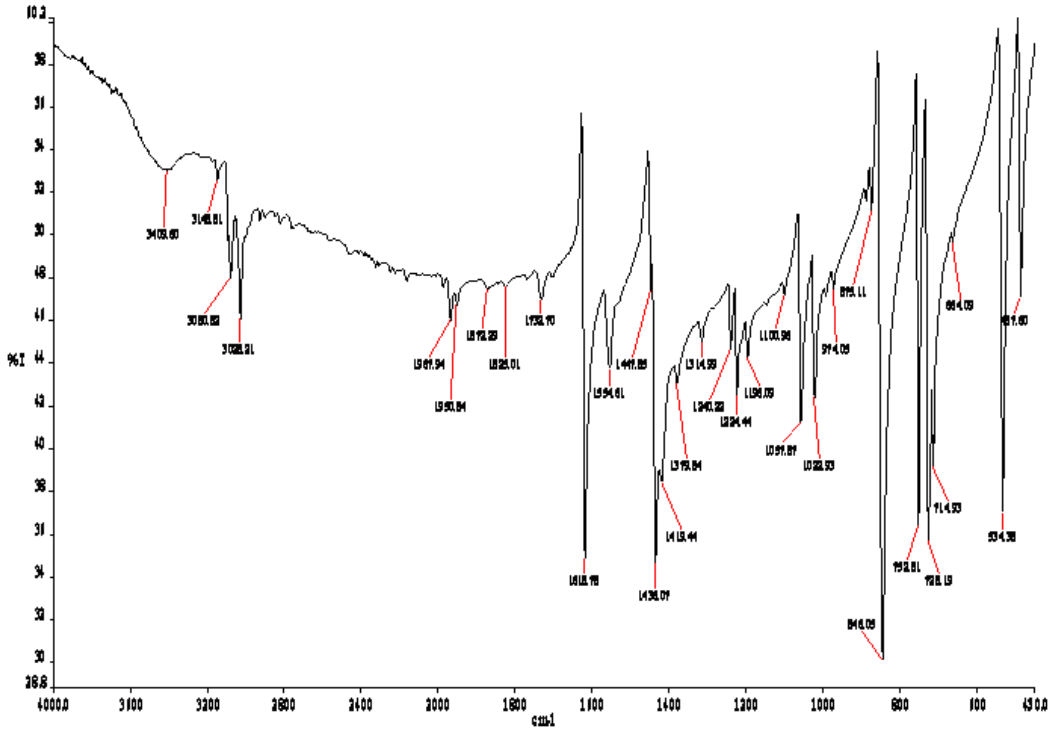


Fig. S6 IR spectrum of **2**.

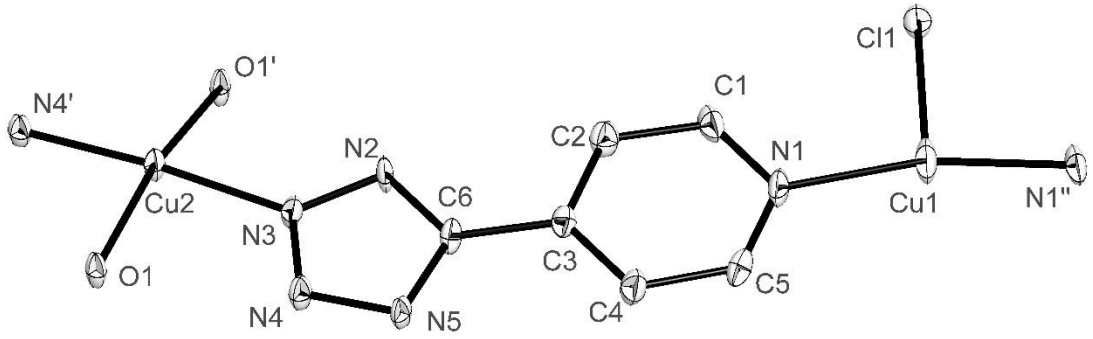


Fig. S7 Structural drawing showing ADPs of **1**. The asymmetric unit of **1** with displacement ellipsoids drawn at 50% probability level. The H atoms are all omitted. (Symmetry code: ‘: (0.5 − *x*, −0.5 + *y*, 0.5 − *z*); ‘‘: (1−*x*, *y*, 2.5−*z*))

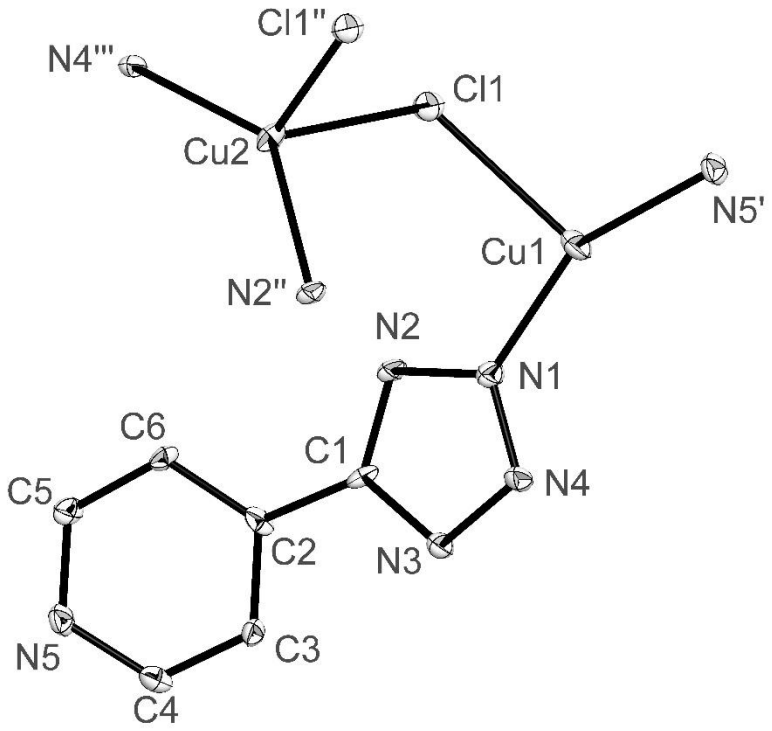


Fig. S8 Structural drawing showing ADPs of **2**. The asymmetric unit of **2** with displacement ellipsoids drawn at 50% probability level. The H atoms are all omitted. (Symmetry code: ′: (−0.5 + *x*, −0.5 + *y*, *z*); ″: (*x*, −1 + *y*, *z*); ‴: (*x*, −1 − *y*, −0.5 + *z*))

Table S1 Crystal data and structure refinement for $[Cu_3Cl(4\text{-pt})_2(OH)_2]_n$ (**1**).

Identification code	10603a	
Empirical formula	C12 H10 Cl Cu3 N10 O2	
Formula weight	552.37	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C* 2/*c*	
Unit cell dimensions	*a* = 12.0666(4) Å	α = 90°
	b = 6.6817(2) Å	β = 107.439(2)°
	c = 20.6749(7) Å	γ = 90°
Volume	1590.30(9) $Å^3$	
Z	4	
Density (calculated)	2.307 Mg/m^3	
Absorption coefficient	4.181 mm^{-1}	
F(000)	1088	
Crystal size	0.24 x 0.15 x 0.12 mm^3	
Theta range for data collection	2.065 to 25.034°	
Index ranges	-14<=h<=13, -7<=k<=7, -21<=l<=24	
Reflections collected	6143	
Independent reflections	1395 [*R*(int) = 0.0812]	
Completeness to theta = 25.03°	99.5%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6878 and 0.5133	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1395 / 1 / 132	
Goodness-of-fit on F^2	1.136	
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0428, w*R*2 = 0.1129	
R indices (all data)	*R*1 = 0.0480, w*R*2 = 0.1286	
Largest diff. peak and hole	0.884 and -1.369 $e.Å^{-3}$	

Table S2 Bond lengths [Å] and angles [°] for $[Cu_3Cl(4\text{-pt})_2(OH)_2]_n$ (**1**).

Cu(1)-N(1)#1	1.937(5)
Cu(1)-N(1)	1.937(5)
Cu(1)-Cl(1)	2.643(2)
Cu(2)-O(1)	1.895(4)
Cu(2)-O(1)#2	1.902(4)
Cu(2)-N(4)#2	1.995(5)
Cu(2)-N(3)	1.997(5)
C(1)-N(1)	1.353(10)
C(1)-C(2)	1.387(9)
C(1)-H(1)	0.9500
C(2)-C(3)	1.395(10)
C(2)-H(2)	0.9500
C(3)-C(4)	1.386(9)
C(3)-C(6)	1.460(8)
C(4)-C(5)	1.396(9)
C(4)-H(4)	0.9500
C(5)-N(1)	1.343(9)
C(5)-H(5)	0.9500
C(6)-N(2)	1.340(8)
C(6)-N(5)	1.357(8)
N(2)-N(3)	1.321(7)
N(3)-N(4)	1.323(8)
N(4)-N(5)	1.341(7)
O(1)-H(1O)	0.84(2)
N(1)#1-Cu(1)-N(1)	162.4(4)
N(1)#1-Cu(1)-Cl(1)	98.82(18)
N(1)-Cu(1)-Cl(1)	98.82(18)
O(1)-Cu(2)-O(1)#2	165.67(5)
O(1)-Cu(2)-N(4)#2	93.99(19)
O(1)#2-Cu(2)-N(4)#2	86.80(19)
O(1)-Cu(2)-N(3)	85.9(2)
O(1)#2-Cu(2)-N(3)	91.7(2)
N(4)#2-Cu(2)-N(3)	173.1(3)
N(1)-C(1)-C(2)	121.7(7)
N(1)-C(1)-H(1)	119.1

C(2)-C(1)-H(1)	119.1
C(1)-C(2)-C(3)	120.2(7)
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-H(2)	119.9
C(4)-C(3)-C(2)	117.8(6)
C(4)-C(3)-C(6)	123.1(6)
C(2)-C(3)-C(6)	119.1(6)
C(3)-C(4)-C(5)	119.3(6)
C(3)-C(4)-H(4)	120.3
C(5)-C(4)-H(4)	120.3
N(1)-C(5)-C(4)	122.6(6)
N(1)-C(5)-H(5)	118.7
C(4)-C(5)-H(5)	118.7
N(2)-C(6)-N(5)	112.4(5)
N(2)-C(6)-C(3)	122.4(6)
N(5)-C(6)-C(3)	125.2(6)
C(5)-N(1)-C(1)	118.4(5)
C(5)-N(1)-Cu(1)	123.6(4)
C(1)-N(1)-Cu(1)	118.1(5)
N(3)-N(2)-C(6)	104.2(5)
N(2)-N(3)-N(4)	110.4(5)
N(2)-N(3)-Cu(2)	127.3(5)
N(4)-N(3)-Cu(2)	122.1(4)
N(3)-N(4)-N(5)	110.0(5)
N(3)-N(4)-Cu(2)#3	119.7(4)
N(5)-N(4)-Cu(2)#3	130.4(4)
N(4)-N(5)-C(6)	103.0(5)
Cu(2)-O(1)-Cu(2)#3	125.4(2)
Cu(2)-O(1)-H(1O)	117(6)
Cu(2)#3-O(1)-H(1O)	117(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, y, -z+5/2 #2 -x+1/2, y-1/2, -z+3/2 #3 -x+1/2, y+1/2, -z+3/2

Scheme S1 Bond valence method.* Mixed-valence characteristics of compound **1**.

Bond-Valence-Sum analysis

Cu(1)	Ri	*f1*	*f2*
N(1)	1.94	0.432645	0.600009
N(1a)	1.94	0.432645	0.600009
Cl(1)	2.675	0.109908	0.161327
		0.9752	*1.36134*

Cu(2)	Ri	*f1*	*f2*
N(4b)	2.023	0.345708	0.479441
N(3c)	1.991	0.376938	0.522752
O(1)	1.886	0.35614	0.535623
O(1d)	1.909	0.334675	0.503341
Cl(1)	2.791	0.080329	0.11791
		1.49379	*2.15907*

	Ro(1+)	Bo	Ro(2+)	Bo
Cu-N	1.63	0.37	1.751	0.37
Cu-O	1.504	0.37	1.655	0.37
Cu-Cl	1.858	0.37	2	0.37

Ri: Metal coordination bond distance of crystal structure (Angstrom)
Ro: emperical bonding distance (Angstrom)
Bo: emperical parameter(Angstrom)
f1=exp[(Ro(1+)-Ri)/Bo]
f2=exp[(Ro(2+)-Ri)/Bo]

Based on the Bond-Valence-Sum analysis, Cu(1) is 0.9752 and Cu(2) is 2.1591. Accordingly, Cu(1) presents a +1 charge but Cu(2) presents a +2 charge.

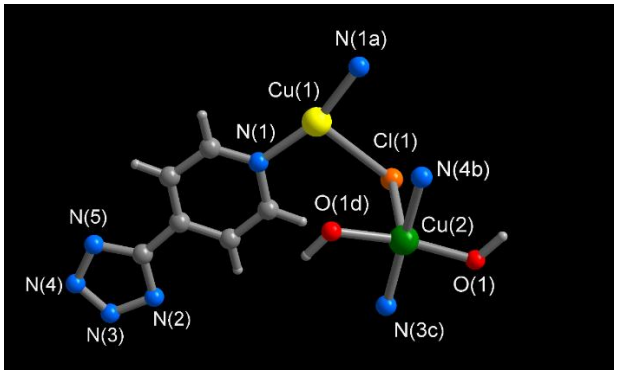


Fig. A view of the metal coordination environment of **1**. (Symmetry code: a: (1−*x*, *y*, 0.5−*z*); b (0.5+*x*, 0.5−*y*, 0.5+*z*); c (1−*x*, 1−*y*, −*z*); d (1.5−*x*, −0.5+*y*, 0.5−*z*)).

*The oxidation states of Cu cations were calculated by "bond valence method" reported by Thorp, H. H., *Inorg. Chem.* **1992**, *31*, 1585–1588. https://pubs.acs.org/doi/pdf/10.1021/ic00035a012

Table S3 Crystal data and structure refinement for $[Cu_2Cl(4\text{-pt})]_n$ (**2**).

Identification code	a11935	
Empirical formula	C6 H4 Cl Cu2 N5	
Formula weight	308.67	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*Cc*	
Unit cell dimensions	*a* = 19.689(5) Å	α = 90°
	b = 3.6236(9) Å	β = 102.953(3)°
	c = 11.631(3) Å	γ = 90°
Volume	808.7(3) $Å^3$	
Z	4	
Density (calculated)	2.535 Mg/m^3	
Absorption coefficient	5.543 mm^{-1}	
F(000)	600	
Crystal size	0.22 x 0.10 x 0.04 mm^3	
Theta range for data collection	2.123 to 25.069°	
Index ranges	-22<=h<=21, -4<=k<=1, -12<=l<=13	
Reflections collected	1437	
Independent reflections	1200 [*R*(int) = 0.0173]	
Completeness to theta = 25.07°	97.8%	
Absorption correction	None	
Max. and min. transmission	0.8087 and 0.3752	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1200 / 2 / 128	
Goodness-of-fit on F^2	1.069	
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0240, w*R*2 = 0.0655	
R indices (all data)	*R*1 = 0.0305, w*R*2 = 0.1018	
Absolute structure parameter	0.38(4)	
Largest diff. peak and hole	0.645 and -0.894 e.$Å^{-3}$	

Table S4 Bond lengths [Å] and angles [°] for $[Cu_2Cl(4\text{-pt})]_n$ (**2**).

Cu(1)-N(1)	1.920(10)
Cu(1)-N(5)#1	1.938(8)
Cu(1)-Cl(1)	2.484(3)
Cu(2)-N(4)#2	1.962(9)
Cu(2)-N(2)#3	2.033(9)
Cu(2)-Cl(1)	2.439(2)
Cu(2)-Cl(1)#3	2.490(2)
C(1)-N(2)	1.347(13)
C(1)-N(3)	1.350(13)
C(1)-C(2)	1.467(13)
C(2)-C(3)	1.384(14)
C(2)-C(6)	1.392(14)
C(3)-C(4)	1.366(15)
C(3)-H(3)	0.9500
C(4)-N(5)	1.350(15)
C(4)-H(4)	0.9500
C(5)-N(5)	1.345(13)
C(5)-C(6)	1.375(15)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
N(1)-N(4)	1.328(14)
N(1)-N(2)	1.341(14)
N(3)-N(4)	1.334(12)
N(1)-Cu(1)-N(5)#1	152.7(4)
N(1)-Cu(1)-Cl(1)	100.7(3)
N(5)#1-Cu(1)-Cl(1)	106.4(3)
N(4)#2-Cu(2)-N(2)#3	133.9(3)
N(4)#2-Cu(2)-Cl(1)	116.0(3)
N(2)#3-Cu(2)-Cl(1)	97.5(2)
N(4)#2-Cu(2)-Cl(1)#3	106.9(3)
N(2)#3-Cu(2)-Cl(1)#3	100.5(2)
Cl(1)-Cu(2)-Cl(1)#3	94.63(9)
Cu(2)-Cl(1)-Cu(1)	123.05(11)
Cu(2)-Cl(1)-Cu(2)#4	94.63(9)
Cu(1)-Cl(1)-Cu(2)#4	78.78(8)

N(2)-C(1)-N(3)	111.2(9)
N(2)-C(1)-C(2)	128.5(9)
N(3)-C(1)-C(2)	120.2(8)
C(3)-C(2)-C(6)	118.0(9)
C(3)-C(2)-C(1)	118.4(8)
C(6)-C(2)-C(1)	123.5(9)
C(4)-C(3)-C(2)	120.4(9)
C(4)-C(3)-H(3)	119.8
C(2)-C(3)-H(3)	119.8
N(5)-C(4)-C(3)	122.1(9)
N(5)-C(4)-H(4)	118.9
C(3)-C(4)-H(4)	118.9
N(5)-C(5)-C(6)	123.6(9)
N(5)-C(5)-H(5)	118.2
C(6)-C(5)-H(5)	118.2
C(5)-C(6)-C(2)	118.4(9)
C(5)-C(6)-H(6)	120.8
C(2)-C(6)-H(6)	120.8
N(4)-N(1)-N(2)	108.9(8)
N(4)-N(1)-Cu(1)	128.2(8)
N(2)-N(1)-Cu(1)	122.6(8)
N(1)-N(2)-C(1)	105.1(9)
N(1)-N(2)-Cu(2)#4	112.2(6)
C(1)-N(2)-Cu(2)#4	141.7(7)
N(4)-N(3)-C(1)	104.6(8)
N(1)-N(4)-N(3)	110.2(9)
N(1)-N(4)-Cu(2)#5	130.1(7)
N(3)-N(4)-Cu(2)#5	119.6(6)
C(5)-N(5)-C(4)	117.4(9)
C(5)-N(5)-Cu(1)#6	123.0(7)
C(4)-N(5)-Cu(1)#6	119.4(7)

Symmetry transformations used to generate equivalent atoms:

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

#4 x, y+1, z #5 x, -y-1, z+1/2 #6 x+1/2, y+1/2, z