Supporting Information

A Stable and Sensitive Organic-Inorganic Hybrid Reversible Thermochromic Material: [1-(2-Fluoroethyl)Piperazine]$_2$[CuCl$_4$]

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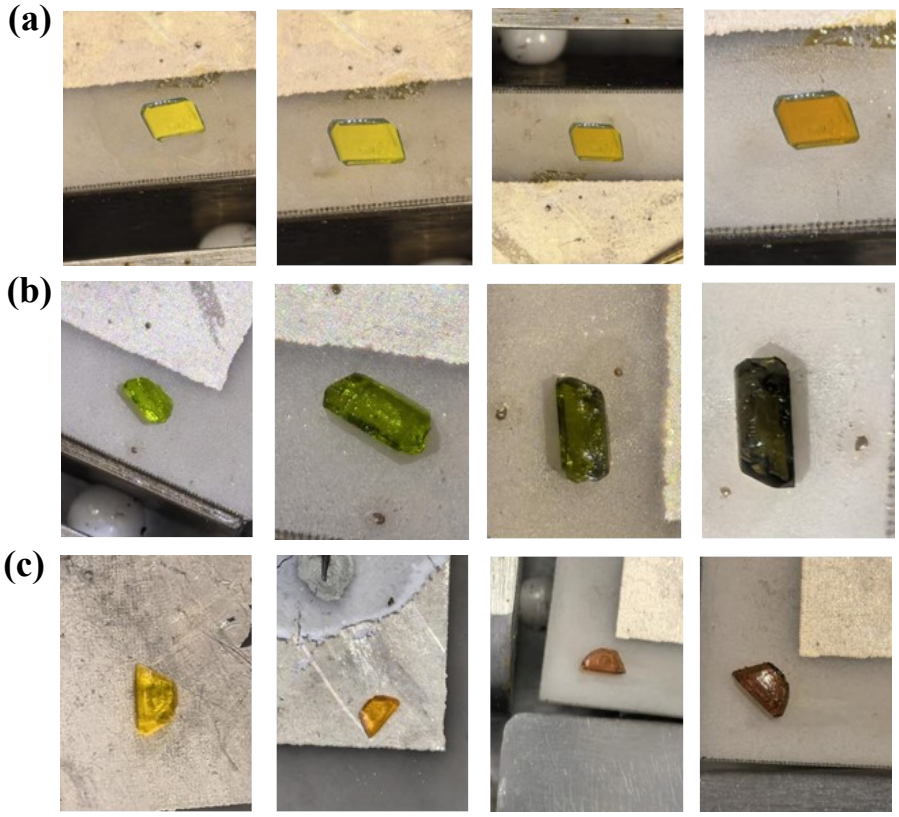

Fig. S1 Temperature-induced reversible color change in (a) [MePZ]$CuCl_4$, (b) [EtPZ]$CuCl_4$ and (c) [FEtPZ]$CuCl_4$.

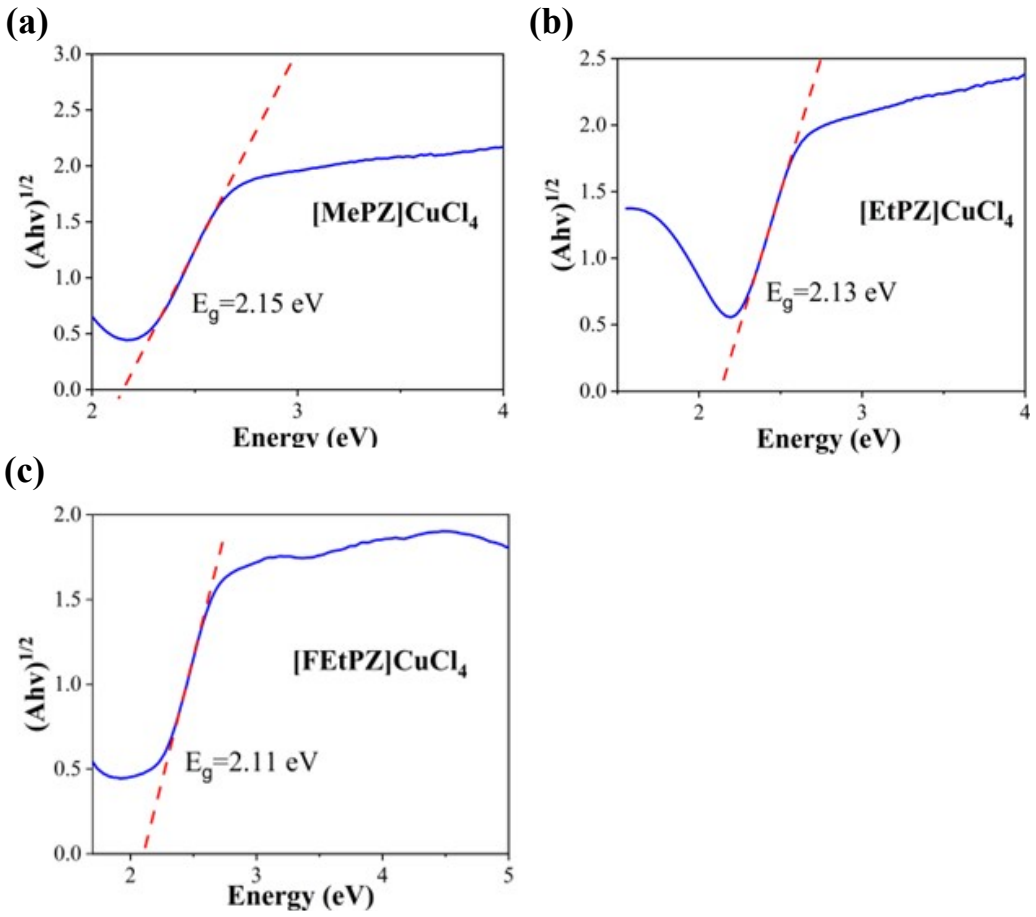

Fig. S2 That shows the Tauc plot for determining the band gap of (a) $[MePZ]CuCl_4$, (b) $[EtPZ]CuCl_4$ and (c) $[FEtPZ]CuCl_4$, with 2.15 eV, 2.13 eV and 2.11 eV.

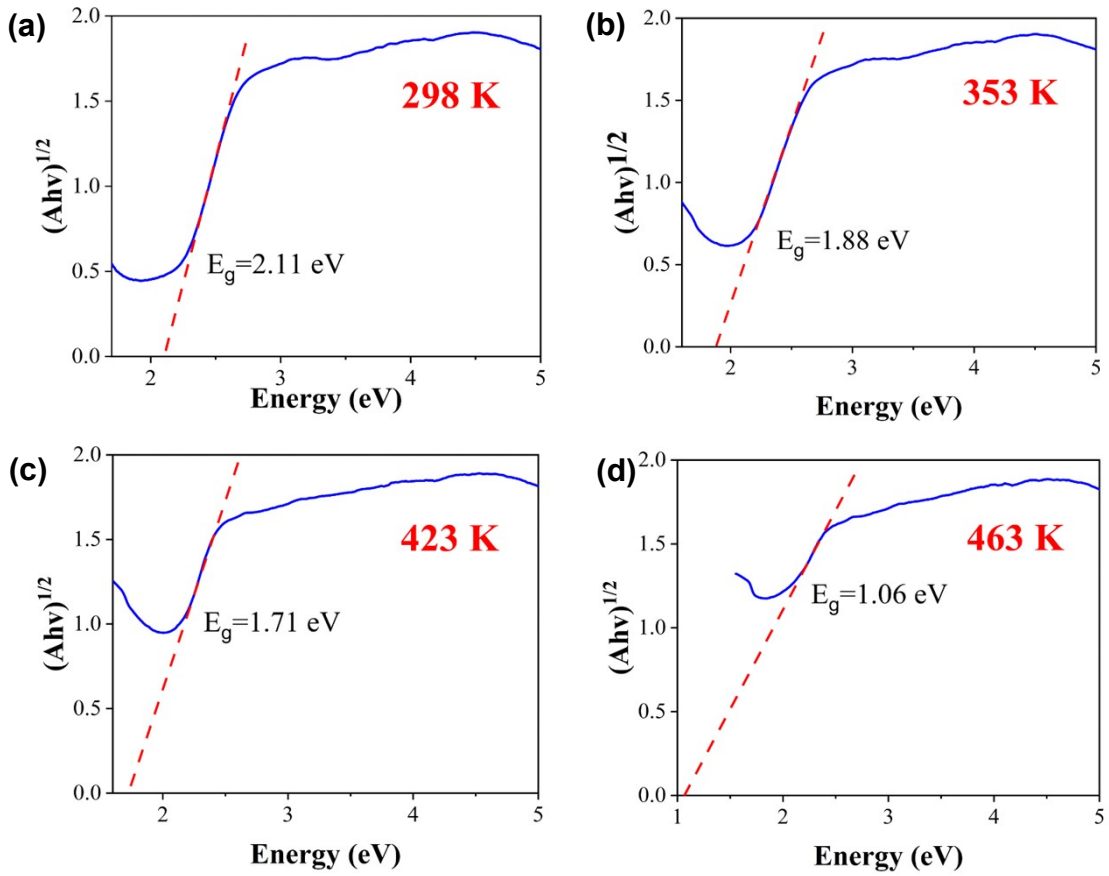

Fig. S3 The figure illustrates the Tauc plots of [FEtPZ]CuCl4 at different temperatures, with panels a, b, c, and d corresponding to temperatures of 298 K, 353 K, 423 K, and 463 K respectively.

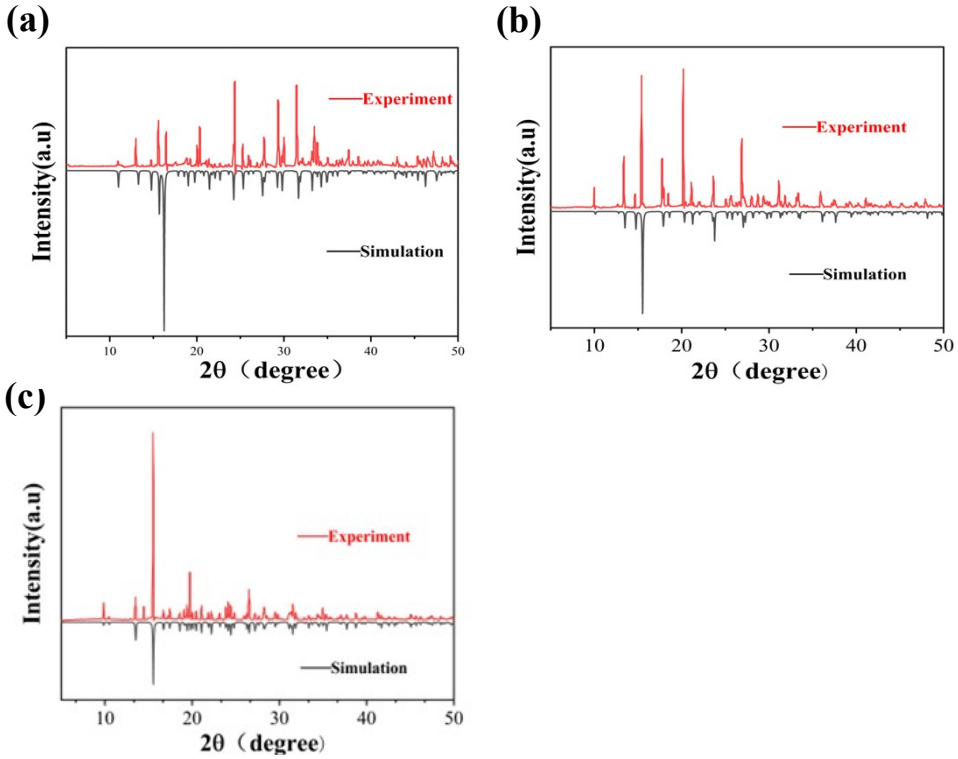

Fig. S4 Experimental powder X-ray diffraction patterns of (a) $[MePZ]CuCl_4$, (b) $[EtPZ]CuCl_4$ and (c) $[FEtPZ]CuCl_4$ match very well with the simulated ones based on the crystal structures at 296 K.

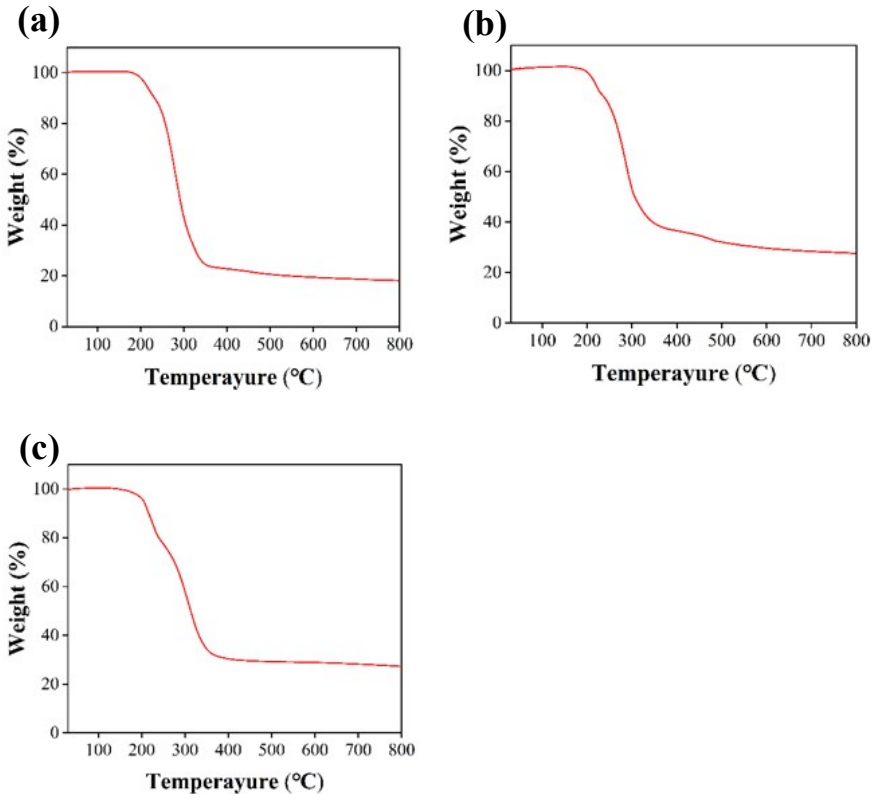

Fig. S5 The TG curves for (a) [MePZ]$CuCl_4$, (b) [EtPZ]$CuCl_4$ and (c) [FEtPZ]$CuCl_4$, indicating the decent thermal stability of the three compounds.

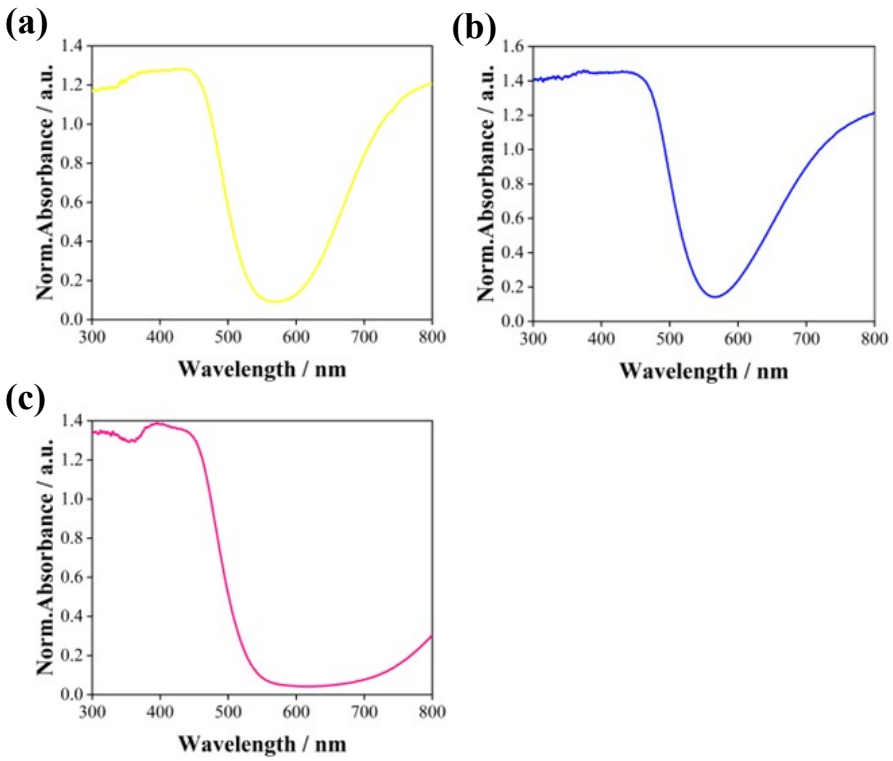

Fig. S6 The ultraviolet-visible spectrum of compound (a) [MePZ]$CuCl_4$, (b) [EtPZ]$CuCl_4$ and (c) [FEtPZ]$CuCl_4$ at room temperature.

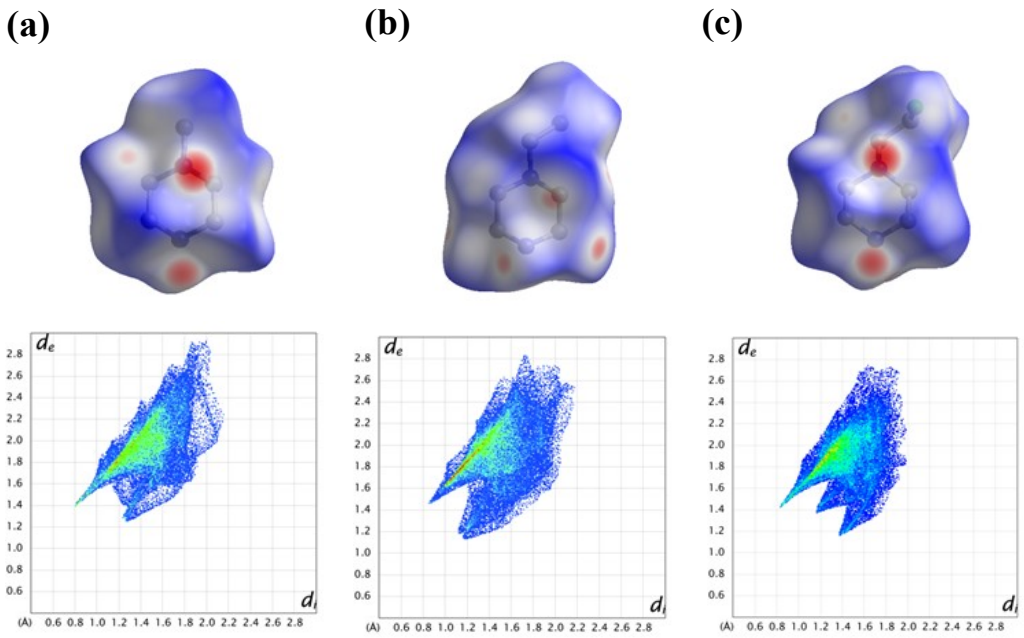

Fig. S7 At 296 K, the close contacts between Allinside···Alloutside of (a) [MePZ]$CuCl_4$, (b) [EtPZ]$CuCl_4$ and (c) [FEtPZ]$CuCl_4$, respectively. The intensity of molecular interaction is mapped onto the Hirshfeld surface by using a red-blue-white color scheme: where the white regions exactly correspond to the distance of Van der Waals contact, the blue regions correspond to longer contacts, and the red regions represent closer contacts. In 2D fingerprint plots, each point represents an individual pair (di, de), reflecting the distances to the nearest atom inside (di) and outside (de) of the Hirshfeld surface, and the frequency of occurrence for these points corresponds to the colors from blue (low), through green, to red (highest).

Formula	[MePZ]$CuCl_4$	[EtPZ]$CuCl_4$	[FEtPZ]$CuCl_4$
Formula weight	307.52	320.54	339.54
Temperature / K	296.15	296.15	296.15
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$
a/Å	8.9767(9)	7.5307(12)	7.5451(5)
b/Å	9.9167(11)	9.9035(17）	17.9299(11)
c/Å	13.7275(16)	17.459(3）	9.7675(5)
α/deg	90	90	90
β/deg	90	90	102.460(4)
γ/deg	90	90	90
Volume/Å	1222.0(2)	1302.1(4)	1290.25(14)
Z	4	4	4
Density g/cm3	1.672	1.635	1.748
R1[I>=2σ(I)]	0.0315	0.0351	0.0298
wR2[I>=2σ(I)]	0.0740	0.0842	0.0721
GOF	1.091	1.006	1.081

Table S1. Crystal data and structure refinements for compounds 1-3 at 296 K.

Table S2. Crystal data and structure refinements for compounds 3 at 400 K.

Formula	[FEtPZ]$CuCl_4$	β/deg	102.956(7)
Formula weight	339.54	γ/deg	90
Temperature/K	400.00	Volume/Å	1311.1(4)
Crystal system	monoclinic	Z	4
Space group	$P2_1/n$	Density g/cm3	1.720
a/Å	7.6236(13)	R1[I>=2σ(I)]	0.0371
b/Å	18.000(3)	wR2[I>=2σ(I)]	0.0897
c/Å	9.8037(16)	GOF	1.094

α/deg	90

Table S3. Hydrogen bonds at 296 K for 1.

D-H...A	D-H	H...A	D...A	<DHA
N(1)-H(1)...Cl(2)	**0.98**	**2.24**	**3.180(3)**	**161**
N(2)-H(2A)...Cl(3)	**0.97**	**2.23**	**3.176(3)**	**164**
N(2)-H(2B)...Cl(1)	**0.97**	**2.42**	**3.175(3)**	**134**
N(2)-H(2B)...Cl(4)	**0.97**	**2.58**	**3.302(3)**	**132**
C(1)-H(1C)...Cl(1)	**0.96**	**2.78**	**3.682(3)**	**157**
C(2)-H(1D)...Cl(1)	**0.97**	**2.77**	**3.435(3)**	**126**
C(3)-H(3B)...Cl(4)	**0.97**	**2.76**	**3.487(3)**	**132**

Table S4. Hydrogen bonds at 296 K for 2.

D-H...A	D-H	H...A	D...A	<DHA
N(1)-H(1)...Cl(1)	**0.86**	**2.71**	**3.241(4)**	**122**
N(1)-H(1)...Cl(2)	**0.86**	**2.60**	**3.209(4)**	**128**
N(0AA)-H(0AA)...Cl(3)	**0.98**	**2.65**	**3.442(3)**	**138**
N(0AA)-H(0AA)...Cl(4)	**0.98**	**2.35**	**3.154(3)**	**139**
C(2)-H(2A)...Cl(3)	**0.97**	**2.80**	**3.542(4)**	**134**
C(2)-H(2B)...Cl(1)	**0.97**	**2.70**	**3.655(4)**	**169**
C(3)-H(3A)...Cl(2)	**0.97**	**2.72**	**3.532(5)**	**142**
C(3)-H(3B)...Cl(3)	**0.97**	**2.82**	**3.688(5)**	**149**
C(6)-H(6A)...Cl(4)	**0.97**	**2.78**	**3.587(4)**	**141**
C(7)-H(7B)...Cl(1)	**0.97**	**2.76**	**3.725(4)**	**172**

Table S5. Hydrogen bonds at 296 K for 3.

D-H...A	D-H	H...A	D...A	<DHA
N(2)-H(2)...Cl(1)	**0.84(3)**	**2.43(3)**	**3.2333(17)**	**160(2)**
N(5)-H(5A)...Cl(2)	**0.89**	**2.77**	**3.3074(18)**	**120**
N(5)-H(5A)...Cl(4)	**0.89**	**2.41**	**3.2488(18)**	**156**
N(5)-H(5B)...Cl(1)	**0.89**	**2.51**	**3.2420(19)**	**140**
N(5)-H(5B)...Cl(2)	**0.89**	**2.62**	**3.2734(17)**	**128**
C(3)-H(3A)...Cl(4)	**0.97**	**2.57**	**3.475(2)**	**155**
C(3)-H(3B)...Cl(4)	**0.97**	**2.76**	**3.535(2)**	**137**

Table S6. Hydrogen bonds at 400 K for 3.

D-H...A	D-H	H...A	D...A	<DHA
N(2)-H(2)...Cl(1)	**0.98**	**2.30**	**3.231(3)**	**158**
N(5)-H(5A)...Cl(2)	**0.89**	**2.79**	**3.328(3)**	**120**
N(5)-H(5A)...Cl(4)	**0.89**	**2.44**	**3.280(3)**	**156**
N(5)-H(5B)...Cl(2)	**0.89**	**2.68**	**3.305(3)**	**128**
N(5)-H(5B)...Cl(1)	**0.89**	**2.52**	**3.255(3)**	**140**
N(2)-H(3B)...Cl(4)	**0.97**	**2.59**	**3.492(4)**	**155**
C(3)-H(3B)...Cl(4)	**0.97**	**2.77**	**3.552(4)**	**138**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cl1	2.2717(10)	C1	H1B	0.9600
Cu1	Cl2	2.2421(11)	C1	H1C	0.9600
Cu1	Cl3	2.2558(11)	C2	H2C	0.9700
Cu1	Cl4	2.2331(11)	C2	H2D	0.9700
N1	H1	0.9800	C2	C3	1.499(6)
N1	C1	1.506(5)	C3	H3A	0.9700
N1	C2	1.492(5)	C3	H3B	0.9700
N1	C4	1.491(5)	C4	H4A	0.9700
N2	H2A	0.9700	C4	H4B	0.9700
N2	H2B	0.9700	C4	C5	1.502(5)
N2	C3	1.491(5)	C5	H5A	0.9700
N2	C5	1.493(5)	C5	H5B	0.9700
C1	H1A	0.9600			

Table S7. Selected Bond Lengths for compound 1 at 296 K.

Table S8. Selected Bond Lengths for compound 2 at 296 K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	**Cl1**	**2.2172(12)**	**C3**	**H3A**	**0.9700**
Cu1	**Cl2**	**2.2548(13)**	**C3**	**H3B**	**0.9700**
Cu1	**Cl3**	**2.2505(11)**	**C4**	**H4A**	**0.9700**
Cu1	**Cl4**	**2.2195(12)**	**C4**	**H4B**	**0.9700**
N0AA	**H0AA**	**0.9800**	**C4**	**C5**	**1.515(9)**
N0AA	**C3**	**1.494(5)**	**C5**	**H5A**	**0.9600**
N0AA	**C4**	**1.490(6)**	**C5**	**H5B**	**0.9600**
N0AA	**C7**	**1.496(6)**	**C5**	**H5C**	**0.9600**
N1	**H1**	**0.8600**	**C6**	**H6A**	**0.9700**
N1	**C2**	**1.473(6)**	**C6**	**H6B**	**0.9700**
N1	**C6**	**1.480(5)**	**C6**	**C7**	**1.493(7)**
C2	**H2A**	**0.9700**	**C7**	**H7A**	**0.9700**
C2	**H2B**	**0.9700**	**C7**	**H7B**	**0.9700**
C2	**C3**	**1.495(6)**			

Table S9. Selected Bond Lengths for compound 3 at 296 K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cl1	2.2920(6)	C3	H3A	0.9700
Cu1	Cl2	2.2379(6)	C3	H3B	0.9700
Cu1	Cl3	2.2062(6)	C3	C4	1.508(3)
Cu1	Cl4	2.2566(6)	C4	H4A	0.9700
F1	C1	1.396(3)	C4	H4B	0.9700
N2	C2	1.502(3)	C4	N5	1.485(3)
N2	C3	1.497(3)	N5	H5A	0.8900
N2	C7	1.500(3)	N5	H5B	0.8900
N2	H2	0.84(3)	N5	C6	1.483(3)
C1	H1A	0.9700	C6	H6A	0.9700
C1	H1B	0.9700	C6	H6B	0.9700
C1	C2	1.494(3)	C6	C7	1.511(3)
C2	H2A	0.9700	C7	H7A	0.9700
C2	H2B	0.9700	C7	H7B	0.9700

Table S10. Selected Bond Lengths for compound 3 at 400 K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cl2	2.2414(10)	C7	H7B	0.9700
Cu1	Cl4	2.2563(11)	C7	C6	1.511(5)
Cu1	Cl1	2.3044(11)	C4	H4A	0.9700
Cu1	Cl3	2.2003(12)	C4	H4B	0.9700
N2	H2	0.9800	C4	C3	1.510(5)
N2	C7	1.501(4)	C3	H3A	0.9700
N2	C3	1.500(4)	C3	H3B	0.9700
N2	C2	1.505(4)	C2	H2A	0.9700
F1	C1	1.383(5)	C2	H2B	0.9700
N5	H5A	0.8900	C2	C1	1.497(5)
N5	H5B	0.8900	C6	H6A	0.9700
N5	C4	1.481(5)	C6	H6B	0.9700
N5	C6	1.475(5)	C1	H1A	0.9700
C7	H7A	0.9700	C1	H1B	0.9700

Table S11. Selected Bond Angles for compound 1 at 296 K.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	Cu1	Cl1	97.50(4)	N1	C2	H2C	109.7
Cl2	Cu1	Cl3	99.41(4)	N1	C2	H2D	109.7
Cl3	Cu1	Cl1	131.02(5)	N1	C2	C3	109.8(3)
Cl4	Cu1	Cl1	95.94(4)	H2C	C2	H2D	108.2
Cl4	Cu1	Cl2	141.56(5)	C3	C2	H2C	109.7
Cl4	Cu1	Cl3	98.44(4)	C3	C2	H2D	109.7
C1	N1	H1	108.1	N2	C3	C2	110.3(3)
C2	N1	H1	108.1	N2	C3	H3A	109.6
C2	N1	C1	112.4(3)	N2	C3	H3B	109.6
C2	N1	C4	109.7(3)	C2	C3	H3A	109.6
C4	N1	H1	108.1	C2	C3	H3B	109.6
C4	N1	C1	110.3(3)	H3A	C3	H3B	108.1
H2A	N2	H2B	107.9	N1	C4	H4A	109.6
C3	N2	H2A	109.2	N1	C4	H4B	109.6
C3	N2	H2B	109.2	N1	C4	C5	110.4(3)
C3	N2	C5	112.0(3)	H4A	C4	H4B	108.1
C5	N2	H2A	109.2	C5	C4	H4A	109.6
C5	N2	H2B	109.2	C5	C4	H4B	109.6
N1	C1	H1A	109.5	N2	C5	C4	110.9(3)
N1	C1	H1B	109.5	N2	C5	H5A	109.5
N1	C1	H1C	109.5	N2	C5	H5B	109.5
H1A	C1	H1B	109.5	C4	C5	H5A	109.5
H1A	C1	H1C	109.5	C4	C5	H5B	109.5
H1B	C1	H1C	109.5	H5A	C5	H5B	108.0

Table S12. Selected Bond Angles for compound 2 at 296 K.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Cu1	Cl2	96.34(5)	H3A	C3	H3B	107.9
Cl1	Cu1	Cl3	141.72(5)	N0AA	C4	H4A	109.0
Cl1	Cu1	Cl4	97.78(5)	N0AA	C4	H4B	109.0
Cl3	Cu1	Cl2	95.92(5)	N0AA	C4	C5	113.1(5)
Cl4	Cu1	Cl2	139.68(6)	H4A	C4	H4B	107.8
Cl4	Cu1	Cl2	95.90(5)	C5	C4	H4A	109.0
C3	N0AA	H0AA	107.9	C5	C4	H4B	109.0
C3	N0AA	C7	110.0(3)	C4	C5	H5A	109.5
C4	N0AA	H0AA	107.9	C4	C5	H5B	109.5
C4	N0AA	C3	112.5(4)	C4	C5	H5C	109.5
C4	N0AA	C7	110.6(4)	H5A	C5	H5B	109.5
C7	N0AA	H0AA	107.9	H5A	C5	H5C	109.5
C2	N1	H1	124.5	H5B	C5	H5C	109.5
C2	N1	C6	111.1(3)	N1	C6	H6A	109.7
C6	N1	H1	124.5	N1	C6	H6B	109.7
N1	C2	H2A	109.3	N1	C6	C7	109.6(4)
N1	C2	H2B	109.3	H6A	C6	H6B	108.2
N1	C2	C3	111.5(4)	C7	C6	H6A	109.7
H2A	C2	H2B	108.0	C7–C	C6	H6B	109.7
C3	C2	H2A	109.3	N0AA	C7	H7A	109.4
C3	C2	H2B	109.3	N0AA	C7	H7B	109.4
N0AA	C3	C2	112.2(4)	C6	C7	N0AA	111.1(3)
N0AA	C3	H3A	109.2	C6	C7	H7A	109.4
N0AA	C3	H3B	109.2	C6	C7	H7B	109.4
C2	C3	H3A	109.2	H7A	C7	H7B	108.0
C2	C3	H3B	109.2				

Table S13. Selected Bond Angles for compound 3 at 296 K.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	Cu1	Cl1	99.96(2)	H3A	C3	H3B	107.8
Cl2	Cu1	Cl4	98.14(2)	C4	C3	H3A	109.1
Cl3	Cu1	Cl1	102.55(3)	C4	C3	H3B	109.1
Cl3	Cu1	Cl2	134.34(3)	C3	C4	H4A	109.5
Cl3	Cu1	Cl4	103.63(3)	C3	C4	H4B	109.5
Cl4	Cu1	Cl1	120.53(3)	H4A	C4	H4B	108.1
C2	N2	H2	109.5(17)	N5	C4	C3	110.55(17)
C3	N2	C2	111.92(16)	N5	C4	H4A	109.5
C3	N2	C7	111.55(15)	N5	C4	H4B	109.5
C3	N2	H2	106.1(17)	C4	N5	H5A	109.5
C7	N2	C2	109.27(15)	C4	N5	H5B	109.5
C7	N2	H2	108.4(17)	H5A	N5	H5B	108.0
F1	C1	H1A	109.9	C6	N5	C4	110.90(16)
F1	C1	H1B	109.9	C6	N5	H5A	109.5
F1	C1	C2	109.1(2)	C6	N5	H5B	109.5
H1A	C1	H1B	108.3	N5	C6	H6A	109.6
C2	C1	H1A	109.9	N5	C6	H6B	109.6
C2	C1	H1B	109.9	N5	C6	C7	110.44(17)
N2	C2	H2A	108.9	H6A	C6	H6B	108.1
N2	C2	H2B	108.9	C7	C6	H6A	109.6
C1	C2	N2	113.57(18)	C7	C6	H6B	109.6
C1	C2	H2A	108.9	N2	C7	C6	112.19(17)
C1	C2	H2B	108.9	N2	C7	H7A	109.2
H2A	C2	H2B	107.7	N2	C7	H7B	109.2
N2	C3	H3A	109.1	C6	C7	H7A	109.2
N2	C3	H3B	109.1	C6	C7	H7B	109.2
N2	C3	C4	112.54(17)	H7A	C7	H7B	107.9

Table S14. Selected Bond Angles for compound 3 at 400 K.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	Cu1	Cl4	98.66(4)	C3	C4	H4A	109.6
Cl2	Cu1	Cl1	100.39(4)	C3	C4	H4B	109.6
Cl4	Cu1	Cl1	119.01(5)	N2	C3	C4	112.4(3)
Cl3	Cu1	Cl2	133.32(5)	N2	C3	H3A	109.1
Cl3	Cu1	Cl4	104.19(5)	N2	C3	H3B	109.1
Cl3	Cu1	Cl1	103.05(5)	C4	C3	H3A	109.1
C7	N2	H2	108.0	C4	C3	H3B	109.1
C7	N2	C2	109.2(3)	H3A	C3	H3B	107.9
C3	N2	H2	108.0	N2	C2	H2A	108.8
C3	N2	C7	111.4(3)	N2	C2	H2B	108.8
C3	N2	C2	112.3(3)	H2A	C2	H2B	107.7
C2	N2	H2	108.0	C1	C2	N2	113.7(3)
H5A	N5	H5B	108.0	C1	C2	H2A	108.8
C4	N5	H5A	109.3	C1	C2	H2B	108.8
C4	N5	H5B	109.3	N5	C6	C7	110.4(3)
C6	N5	H5A	109.3	N5	C6	H6A	109.6
C6	N5	C4	111.5(3)	N5	C6	H6B	109.6
N2	C7	H7A	109.2	C7	C6	H6A	109.6
N2	C7	H7B	109.2	C7	C6	H6B	109.6
N2	C7	C6	112.1(3)	H6A	C6	H6B	108.1
H7A	C7	H7B	107.9	F1	C1	C2	109.2(3)
C6	C7	H7A	109.2	F1	C1	H1A	109.8
C6	C7	H7B	109.2	F1	C1	H1B	109.8
N5	C4	H4B	109.6	C2	C1	H1A	109.8
N5	C4	H4B	109.6	C2	C1	H1B	109.8
N5	C4	C3	110.4(3)	H1A	C1	H1B	108.3
H4A	C4	H4B	108.1				

Table S15. Torsion angles for compound 1 at 296 K.

Atom	Atom	Atom	Atom	Torsion Angle/°
N1	C2	C3	N2	−58.3(2)
N1	C4	C5	N2	55.5(2)
C	N1	C2	C3	−176.0(3)
C1	N1	C4	C5	176.2(3)
C2	N1	C4	C5	−59.4(4)
C3	N2	C5	C4	−53.9(4)
C4	N1	C2	C3	60.8(4)
C5	N2	C3	C2	55.2(4)

Table S16. Torsion angles for compound 2 at 296 K.

Atom	Atom	Atom	Atom	Torsion Angle/°
N1	C2	C3	N0AA	−53.6(5)
N1	C6	C7	N0AA	59.2(5)
C2	N1	C6	C7	−58.7(5)
C3	N0AA	C4	C5	65.4(6)
C3	N0AA	C7	C6	−56.3(5)
C4	N0AA	C3	C2	177.0(4)
C4	N0AA	C7	C6	178.9(4)
C6	N1	C2	C3	56.1(5)
C7	N0AA	C3	C2	53.3(5)
C7	N0AA	C4	C5	−171.3(4)

Atom	Atom	Atom	Atom	Torsion Angle/°
F1	C1	C2	N2	−57.1(3)
N2	C3	C4	N5	54.6(2)
C2	N2	C3	C4	−173.92(17)
C2	N2	C7	C6	175.65(17)
C3	N2	C2	C1	−55.9(2)
C3	N2	C7	C6	51.4(2)
C3	C4	N5	C6	−58.3(2)
C4	N5	C6	C7	58.7(2)
N5	C6	C7	N2	−55.3(2)
C7	N2	C2	C1	−179.94(19)
C7	N2	C3	C4	−51.1(2)

Table S17. Torsion angles for compound 3 at 296 K.

Table S18. Torsion angles for compound 3 at 400 K.

Atom	Atom	Atom	Atom	Torsion Angle/°
N2	C7	C6	N5	−55.2(4)
N2	C2	C1	F1	−57.5(5)
N5	C4	C3	N2	54.4(4)
C7	N2	C3	C4	−51.5(4)
C7	N2	C2	C1	179.8(3)
C4	N5	C6	C7	58.4(4)
C3	N2	C7	C6	51.7(4)
C3	N2	C2	C1	−56.2(4)
C2	N2	C7	C6	176.2(3)
C2	N2	C3	C4	−174.3(3)
C6	N5	C4	C3	−58.0(4)