New Ionic Liquids of N,N'-Dialkylbenzimidazolium Salt Comprising Copper(II) Ions

Support information

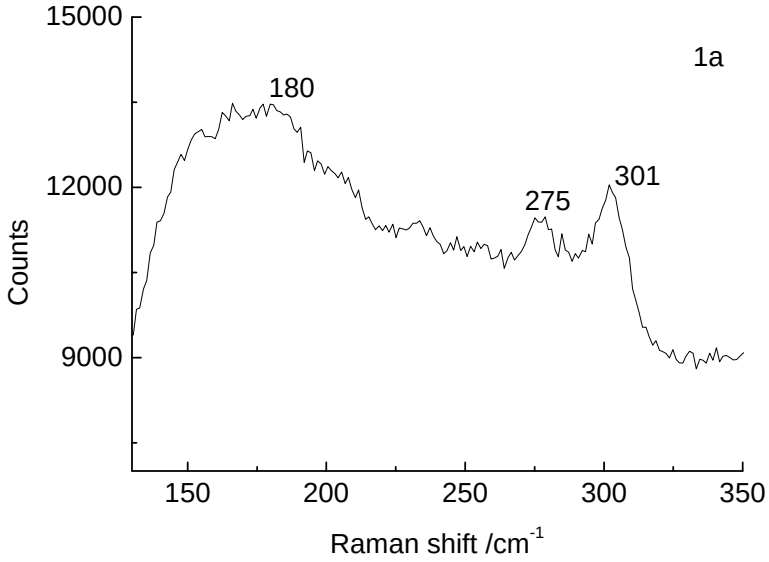

Figure s1. Raman Spectra of **1a**

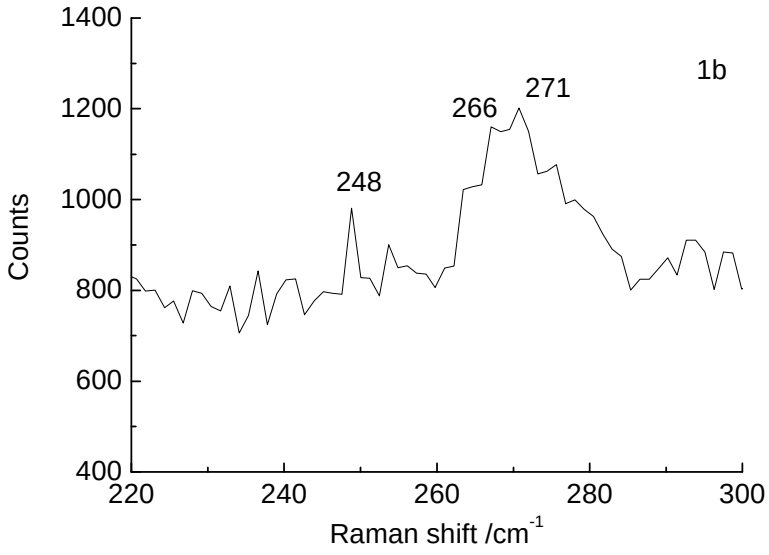

Figure s2. Raman Spectra of **1b**

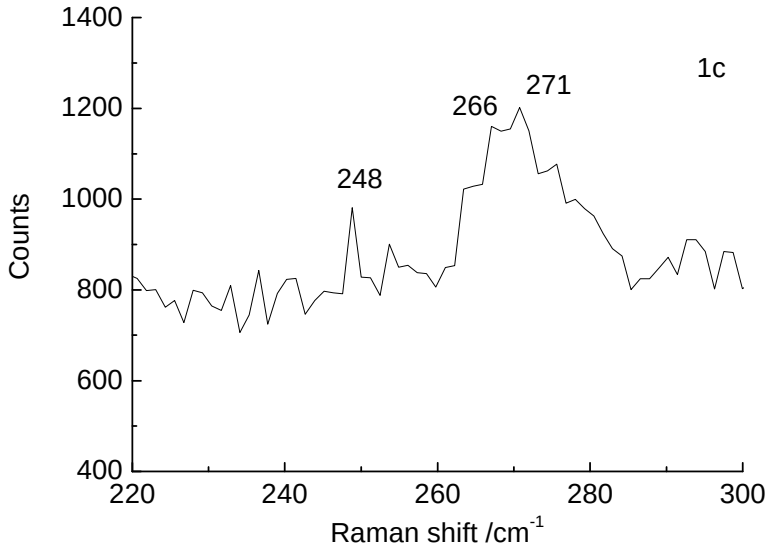

Figure s3. Raman Spectra of **1c**

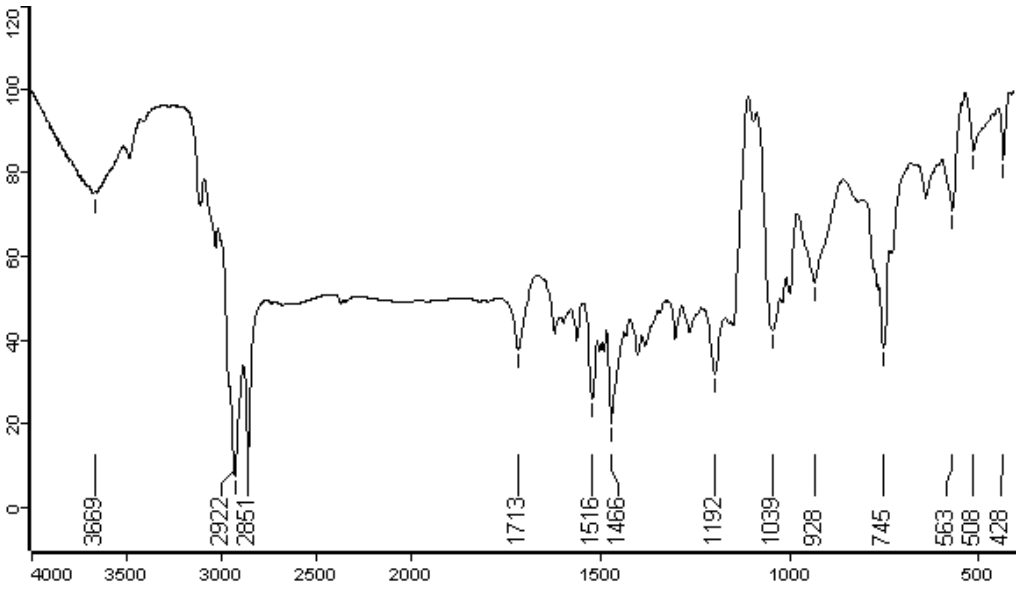

Figure s4. IR Spectra of **1a**

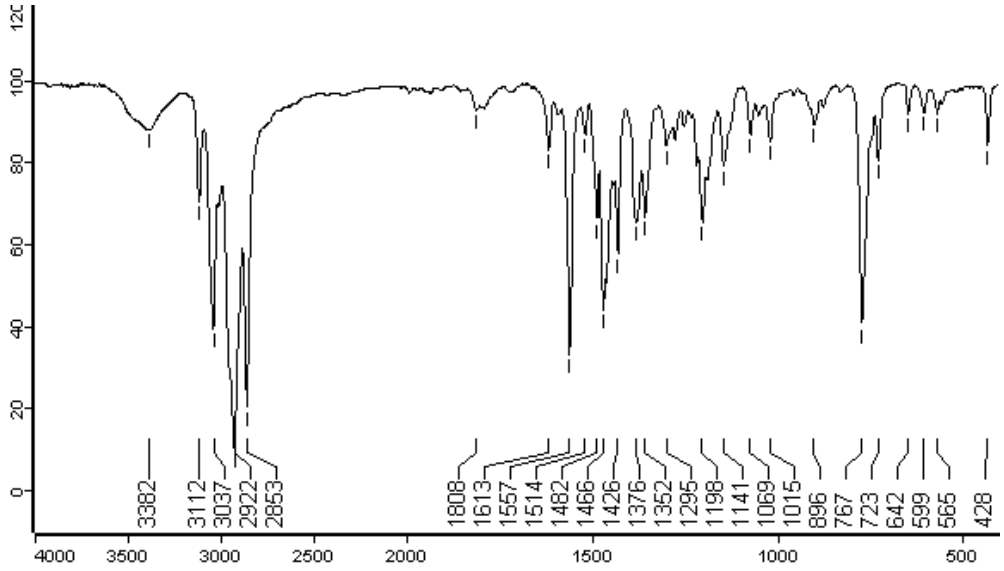

Figure s5. IR Spectra of **1b**

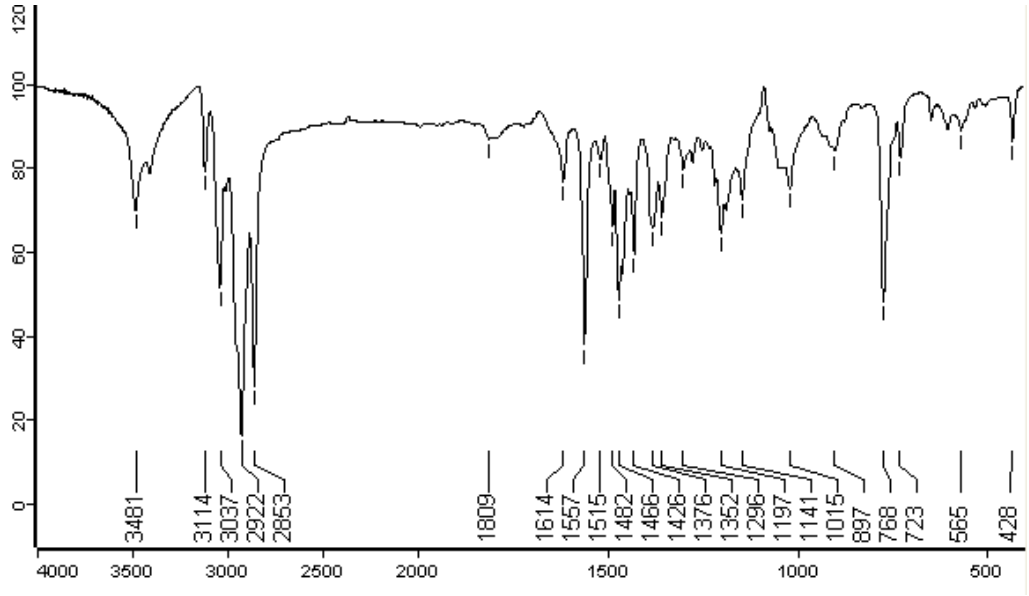

Figure s6. IR Spectra of **1c**

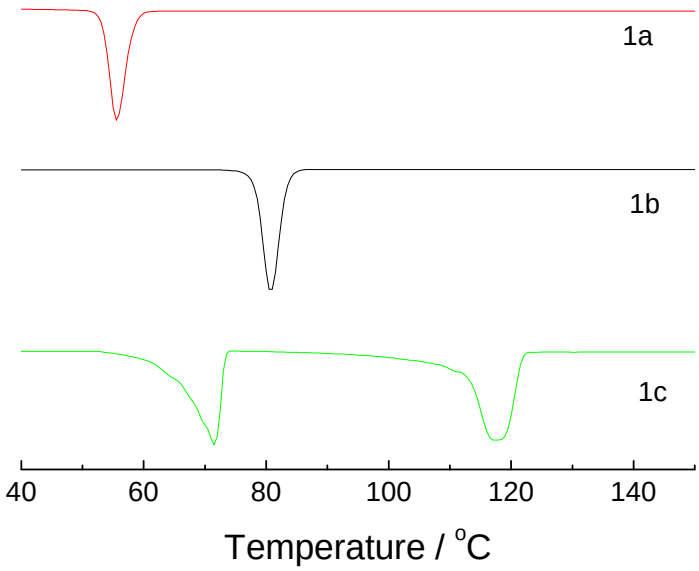

Figure s7. Differential scanning calorimetry results curve (5 K·min^{-1}) of cooling the series of

1a-1c

The TG/DTG curves of **1a** were presented in Fig. 3. We can see that there were two main steps of weight loss, and the decomposition events mainly took place at 194 ºC, and 380 ºC, and.lost most of the weight. **1a** maybe start decomposition at 100°C, although it was no peak. From the weight loss it can suggest that the residue may be Cu(found 5.83 % calcd. 5.69 %).

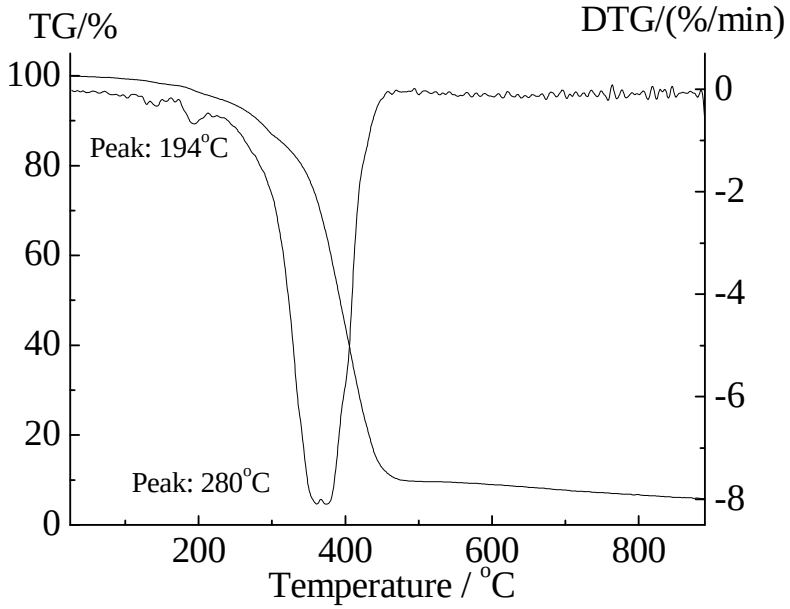

Figure s8.DG-DTG curve (10 K min^{-1}) of **1a**

The TG/DTG curves of **1b** were presented in Fig. 3. We can see that there were two main steps of weight loss, and the decomposition events mainly took place at 205

ºC, and 364 ºC, and.lost most of the weight. **1b** maybe start decomposition at 170°C, although it was no peak. From the weight loss it can suggest that the residue may be Cu (found 6.68 % calcd. 6.32 %).

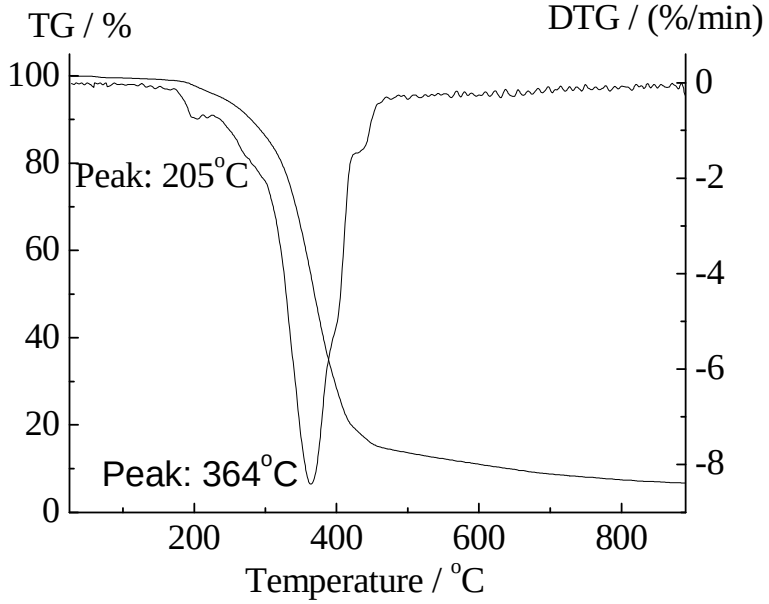

Figure s9.DG-DTG curve (10 K min^{-1}) of **1b**

The TG/DTG curves of **1c** were presented in Fig. 3. We can see that there were three main steps of weight loss, and the decomposition events mainly took place at 248 ºC, 348 ºC and 512 ºC, and.lost most of the weight. **1c** maybe start decomposition at 170°C, although it was no peak. From the weight loss it can suggest that the residue may be Cu (found 6.92 % calcd. 7.12 %).

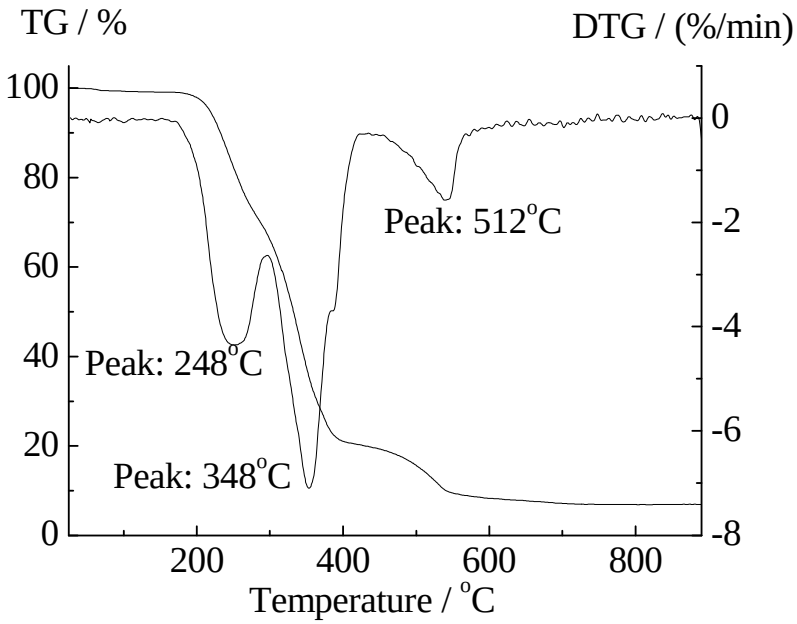

Figure s10. DG-DTG curve (10 K min^{-1}) of **1c**

The TG residues were examined using a X-ray diffraction, and the results showed that the TG residues were copper.

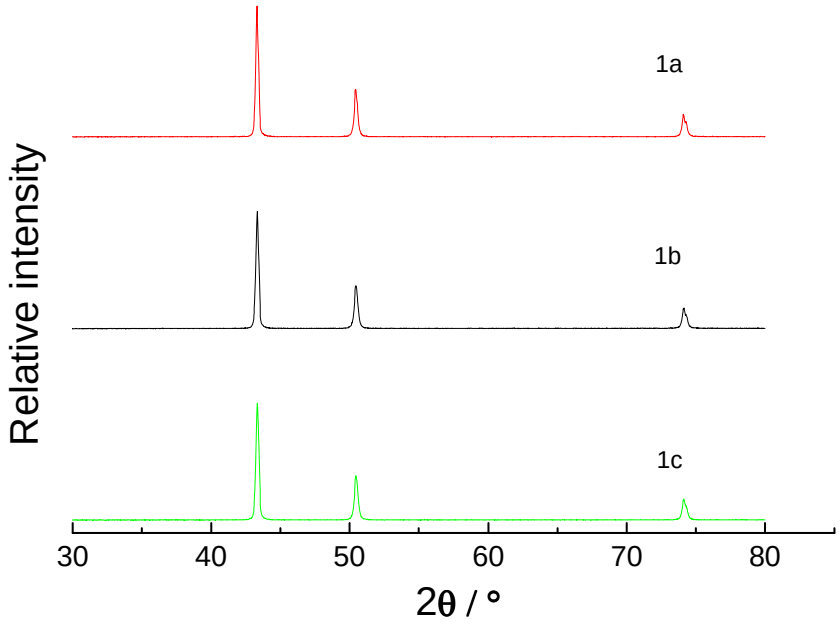

Figure s11. XRD patterns of the TG residues of **1a-1c**

Water Content

The water content was analyzed by Karl-Fischer titration technique (method TitroLine KF). Samples of all compounds were dissolved in methanol and titrated with steps of 2.5µl. The results show a water content ranging from 230 to 280.

Table s1 Selected bond length(Å) and bond angles(°) of **1a**

Cu(1)-Cl(2)$^{\#1}$	2.247(1)	Cl(2)$^{\#1}$-Cu(1)-Cl(2)	180
Cu(1)-Cl(2)	2.247(1)	Cl(2)$^{\#1}$-Cu(1)-Cl(1)$^{\#1}$	90.10(4)
Cu(1)-Cl(1)$^{\#1}$	2.247(1)	Cl(2)-Cu(1)-Cl(1)$^{\#1}$	89.90(4)
Cu(1)-Cl(1)	2.247(1)	Cl(2)$^{\#1}$-Cu(1)-Cl(1)	89.90(4)
N(1)-C(25)	1.320(3)	Cl(2)-Cu(1)-Cl(1)	90.10(4)
N(1)-C(26)	1.384(3)	Cl(1)$^{\#1}$-Cu(1)-Cl(1)	180
N(1)-C(12)	1.465(3)	C(25)-N(1)-C(26)	108.0(2)
N(2)-C(25)	1.324(3)	C(25)-N(1)-C(12)	126.4(2)
N(2)-C(31)	1.386(3)	C(26)-N(1)-C(12)	125.6(2)
N(2)-C(24)	1.469(3)	C(25)-N(2)-C(31)	107.9(2)
N(2)-C(24)-C(23)	111.0(2)	C(25)-N(2)-C(24)	126.4(2)
N(1)-C(25)-N(2)	110.7(2)	C(31)-N(2)-C(24)	125.5(2)

Table s2 Hydrogen-band geometry(Å °) of **1a**

D - H···A	D - H	H···A	D···A	D - H···A
C(12) -H(12A) ···Cl(2)	0.97	2.73	3.6260	153
C(24) -H(24A) ···Cl(2)	0.97	2.81	3.6270	143
C(24) -H(24B) ···Cl(1)	0.97	2.79	3.6817	153
C(25) -H(25A) ···Cl(1)	0.93	2.77	3.5814	146
C(27) -H(27A) ···Cl(1)	0.93	2.75	3.6683	171

Table s3 Selected bond length(Å) and bond angles(°) of IL of **1b**

Cu(1)-Cl(2)	2.280(5)	Cl(2)-Cu(1)-Cl(3)	95.3(2)
Cu(1)-Cl(3)	2.281(4)	Cl(2)-Cu(1)-Cl(1)	141.3(2)
Cu(1)-Cl(1)	2.287(4)	Cl(3)-Cu(1)-Cl(1)	94.2(2)
Cu(1)-Cl(4)	2.290(3)	Cl(2)-Cu(1)-Cl(4)	98.1(2)
N(1)-C(21)	1.35(2)	Cl(3)-Cu(1)-Cl(4)	143.3(2)
N(1)-C(27)	1.39(2)	Cl(1)-Cu(1)-Cl(4)	96.4(2)
N(1)-C(10)	1.51(2)	C(21)-N(1)-C(27)	115(2)
N(2)-C(21)	1.37(2)	C(21)-N(1)-C(10)	122(2)
N(2)-C(22)	1.42(2)	C(27)-N(1)-C(10)	124(2)
N(2)-C(20)	1.48(1)	C(21)-N(2)-C(22)	111(1)
N(3)-C(48)	1.39(2)	C(21)-N(2)-C(20)	126(2)
N(3)-C(54)	1.43(2)	C(22)-N(2)-C(20)	123(2)
N(3)-C(37)	1.46(2)	N(2)-C(20)-C(19)	111(1)
N(4)-C(48)	1.38(1)	N(1)-C(21)-N(2)	105(2)
N(4)-C(47)	1.42(2)	N(4)-C(49)-C(54)	103(2)
N(4)-C(49)	1.42(2)	N(4)-C(49)-C(50)	133(2)

Table s4 Hydrogen-band geometry(Å °) of **1b**

D - H···A	D - H	H···A	D···A	D - H···A
C(10)-H(10A) ··Cl(3)	0.97	2.79	3.6048	142
C(20)-H(20A) ··Cl(2)	0.97	2.74	3.6061	149
C(21)-H(21A ··Cl(1)	0.93	2.77	3.5948	149
C(26)-H(26A) ··Cl(2)	0.93	2.78	3.6846	165
C(37)-H(37B) ··Cl(4)	0.97	2.80	3.6472	146

C(47)-H(47B) ··Cl(4)	0.97	2.78	3.7296	167
C(48)-H(48A) ··Cl(4)	0.93	2.62	3.4533	149
C(53)-H(53A) ··Cl(4)	0.93	2.67	3.5983	173

Table s5 Selected bond length(Å) and bond angles(°) of IL of **1c**

Cu(1)-Cl(3)	2.258(2)	Cl(3)-Cu(1)-Cl(1)	141.93(8)
Cu(1)-Cl(1)	2.273(2)	Cl(3)-Cu(1)-Cl(4)	94.76(6)
Cu(1)-Cl(4)	2.274(2)	Cl(1)-Cu(1)-Cl(4)	94.72(7)
Cu(1)-Cl(2)	2.279(2)	Cl(3)-Cu(1)-Cl(2)	98.18(7)
N(1)-C(17)	1.327(7)	Cl(1)-Cu(1)-Cl(2)	95.64(7)
N(1)-C(23)	1.403(7)	Cl(4)-Cu(1)-Cl(2)	143.65(8)
N(1)-C(8)	1.469(8)	C(17)-N(1)-C(23)	109.7(5)
N(2)-C(17)	1.352(7)	C(17)-N(1)-C(8)	124.8(6)
N(2)-C(18)	1.387(7)	C(23)-N(1)-C(8)	125.1(5)
N(2)-C(16)	1.458(8)	C(17)-N(2)-C(18)	108.5(5)
N(3)-C(40)	1.344(7)	C(17)-N(2)-C(16)	125.1(5)
N(3)-C(46)	1.364(7)	C(18)-N(2)-C(16)	126.3(5)
N(3)-C(31)	1.481(7)	N(2)-C(16)-C(15)	113.3(7)
N(4)-C(40)	1.327(7)	N(1)-C(17)-N(2)	109.4(5)
N(4)-C(41)	1.415(8)	C(40)-N(3)-C(31)	124.9(5)
N(4)-C(39)	1.454(7)	C(46)-N(3)-C(31)	126.5(5)

Table s6 Hydrogen-band geometry(Å °) of **1c**

D - H··A	D - H	H··A	D··A	D - H··A
C(8)-H(8A) ···Cl(2)	0.97	2.79	3.5988	142
C(16)-H(16A) ···Cl(4)	0.97	2.79	3.6577	149
C(17)-H(17A) ···Cl(1)	0.93	2.75	3.5917	151
C(19)-H(19A) ···Cl(4)	0.93	2.82	3.7267	166
C(29)-H(29B) ···N(3)	0.97	2.60	2.9963	104
C(31)-H(31B) ···Cl(3)	0.97	2.82	3.6728	148
C(37)-H(37B) ···N(4)	0.97	2.55	2.9244	103
C(39)-H(39B) ···Cl(3)	0.97	2.77	3.7048	162
C(40)-H(40A) ···Cl(3)	0.93	2.64	3.4748	150
C(42)-H(42A) ···Cl(3)	0.93	2.66	3.5888	172