

Supporting Information

Cu^{II}-mediated controllable creation of tertiary and quaternary carbon centers: designed assembly and structures of a new class of copper complexes supported by *in situ* generated substituted 1-pyridineimidazo[1,5-a]pyridine ligands

Yanmei Chen, Lei Li, Yanyuan Cao, Jian Wu, Qian Gao, Yahong Li,* Hailiang Hu, Wei Liu, Yonglu Liu, Zhenghui Kang and Jingping Li

Experimental Section

Materials. All reagents and solvents were purchased from commercial sources and used as received without further purification. 3-(pyridin-2-yl)imidazo[1,5-a]pyridine (HPIP) was synthesized according to literature procedures.^[S1] All complexes were synthesized by solvothermal reactions under autogenous pressure.

Synthesis of bis(3-(pyridin-2-yl)imidazo[1,5-a]pyridin-1-yl)methane (L4)

A mixture of HPIP (0.0397 g, 0.2 mmol), formaldehyde (0.10 mmol), and glacial acetic acid (2 mL) was sealed in a 6 mL Pyrex-tube and heated at 125 °C for 2 hours. After cooling to room temperature slowly, yellow needle crystals were obtained. Yield: 0.0118 g (29 %).

The ¹H NMR spectrum of **L4** has been determined.

Synthesis of [L1Co₂Cl₄]·2EtOH (4·2EtOH)

A mixture of HPIP (0.0395 g, 0.2 mmol), formaldehyde (0.05 mmol), CoCl₂·6H₂O (0.0238 g, 0.10 mmol), and ethanol (2 mL) was sealed in a 6 mL Pyrex-tube and heated at 135 °C for 3 days. After cooling to room temperature slowly, brown rod crystals were obtained. Yield: 0.0121 g (21%, based on Co). Elemental anal. (%) Calcd. for C₅₃H₄₄Cl₄Co₂N₁₂O₂: C, 55.81; H, 3.89; N, 14.74; Found: C, 55.24; H, 3.85; N, 15.00.

Synthesis of L4ZnCl₂ (5)

A mixture of HPIP (0.0394 g, 0.2 mmol), formaldehyde (0.10 mmol), ZnCl₂ (0.0138 g, 0.10 mmol), and ethanol (2 mL) was sealed in a 6 mL Pyrex-tube and heated at 125 °C for 3 days. After cooling to room temperature slowly, yellow block crystals were obtained. Yield: 0.0153 g (28 %, based on Zn). Elemental anal. (%) Calcd. for C₂₅H₁₈Cl₂N₆Zn: N, 15.60; C, 55.74; H, 3.37; Found: N, 15.76; C, 55.73; H, 3.28.

[S1] O. Niyomura, Y. Yamaguchi, S. Tamura, M. Minoura and Y. Okamoto. *Chem. Lett.* 2011, **40**, 449-451.

Table S1 Crystal data and structure refinement information for complexes **4**·2EtOH, **5** and **L4**.

	4 ·2EtOH	5	L4
Formula ^a	C ₅₃ H ₄₄ Cl ₄ Co ₂ N ₁₂ O ₂	C ₂₅ H ₁₈ Cl ₂ N ₆ Zn	C ₂₅ H ₁₈ N ₆
<i>M</i> / g·mol ⁻¹ ^a	1140.66	538.72	402.45
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C 2/c	P -1	P 2/c
<i>a</i> / Å	24.935(3)	7.8615(6)	12.8398(18)
<i>b</i> / Å	14.5352(15)	10.7668(8)	5.1086(7)
<i>c</i> / Å	17.7035(19)	14.0784(10)	15.192(2)
<i>α</i> / °	90	73.473(1)	90
<i>β</i> / °	131.687(2)	84.73(2)	105.007(3)
<i>γ</i> / °	90	89.354(1)	90
<i>V</i> / Å ³	4791.7(9)	1137.44(15)	962.5(2)
<i>Z</i>	4	2	2
<i>T</i> /K	296(2)	293(2)	296(2)
<i>λ</i> / Å ^b	0.71073	0.71073	0.71073
<i>ρ</i> _c / g·cm ⁻³	1.581	1.573	1.389
<i>μ</i> / mm ⁻¹	0.974	1.342	0.087
<i>F</i> (000)	2336	548	420
<i>θ</i> range / °	2.79 - 25.00	2.12 - 25.00	2.78 - 28.31
Measd/independent	15882 / 4194	6233 / 3923	6416 / 2378
<i>R</i> _{int} reflections	0.0499	0.0144	0.0215
obsd reflns [<i>I</i> > 2σ (<i>I</i>)]	4194	3923	2378
<i>R</i> ₁ ^c	0.0527	0.0313	0.0401
w <i>R</i> ₂ ^{d,e}	0.1439	0.1106	0.1149
GOF on <i>F</i> ²	1.027	1.105	1.080
(Δ <i>ρ</i>) _{max,min} / e·Å ⁻³	2.665, -0.846	0.496, -0.315	0.180, -0.204

^a Including solvate molecules. ^b Mo Kα radiation. ^c $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$ for observed reflections. ^d $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2] / 3$.
^e $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$ for all data.

Table S2 Selected bond lengths [\AA] and angles [$^\circ$] for complex **1**·2EtOH

Cu(1)-N(2)	1.949 (8)	Cu(1)-N(4)	2.062(9)
Cu(1)-N(5)	1.962(9)	Cu(1)-Cl(1)	2.515(3)
Cu(1)-N(1)	2.025(11)		
N(2)-Cu(1)-N(5)	85.0(3)	N(1)-Cu(1)-Cl(1)	89.8(3)
N(2)-Cu(1)-N(1)	80.8(4)	N(4)-Cu(1)-Cl(1)	92.5(3)
N(5)-Cu(1)-N(1)	163.2(4)	Cu(2)#2-Cl(3)-Cu(2)	91.5(4)
N(2)-Cu(1)-N(4)	161.7(4)	Cl(3)-Cu(2)-Cl(2)	173.4(3)
N(5)-Cu(1)-N(4)	80.9(4)	Cu(3)-Cl(2)-Cu(2)	89.2(3)
N(1)-Cu(1)-N(4)	111.0(4)	Cl(2)-Cu(3)-Cl(4)	160.6(3)
N(2)-Cu(1)-Cl(1)	101.7(3)	Cu(3)#2-Cl(4)-Cu(3)	115.0(4)
N(5)-Cu(1)-Cl(1)	101.8(3)		

Symmetry transformations used to generate equivalent atoms:

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

Table S3 Hydrogen bond lengths [\AA] and angles [$^\circ$] for complex **1**·2EtOH

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
O(1)-H(1)...Cl(1)	0.82	2.56	3.24(3)	141.0
O(1B)-H(1B)...Cl(1)	0.82	2.65	3.12(4)	117.9
C(10)-H(10)...Cl(1)#1	0.93	2.65	3.497(15)	151.3
C(7)-H(7)...Cl(4)	0.93	2.68	3.472(15)	143.6
C(18)-H(18)...Cl(2)#3	0.93	2.77	3.520(16)	138.8

Symmetry transformations used to generate equivalent atoms:

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

Table S4 Selected bond lengths [Å] and angles [°] for complex **2**·2EtOH.

Cu(1)-N(5)#1	1.991(2)	Cu(2)-N(7)#1	2.091(2)
Cu(1)-N(2)	1.992(2)	Cu(3)-Cl(1)#2	2.0809(10)
Cu(1)-N(1)	2.080(2)	Cu(3)-Cl(1)	2.0809(10)
Cu(1)-N(4)#1	2.091(2)	Cu(4)-Cl(3)	2.0720(13)
Cu(2)-N(8)#1	1.998(2)	Cu(4)-Cl(2)	2.0790(14)
Cu(2)-N(8)	1.998(2)	N(5)-Cu(1)#1	1.991(2)
Cu(2)-N(7)	2.091(2)		
N(5)#1-Cu(1)-N(2)	133.36(8)	N(8)#1-Cu(2)-N(7)	80.46(9)
N(5)#1-Cu(1)-N(1)	130.77(9)	N(8)-Cu(2)-N(7)	131.28(9)
N(2)-Cu(1)-N(1)	81.28(8)	N(8)#1-Cu(2)-N(7)#1	131.28(9)
N(5)#1-Cu(1)-N(4)#1	81.15(9)	N(8)-Cu(2)-N(7)#1	80.46(9)
N(2)-Cu(1)-N(4)#1	128.43(9)	N(7)-Cu(2)-N(7)#1	105.63(14)
N(1)-Cu(1)-N(4)#1	104.45(9)	Cl(1)#2-Cu(3)-Cl(1)	178.19(7)
N(8)#1-Cu(2)-N(8)	131.75(12)	Cl(3)-Cu(4)-Cl(2)	175.80(5)
)		
Symmetry transformations used to generate equivalent atoms:			
	#1 -x+1,y,-z+1/2	#2 -x,y,-z+1/2	

Table S5 Hydrogen bond lengths [Å] and angles [°] for complex **2**·2EtOH

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...Cl(2)#3	0.85	2.37	3.175(4)	157.9
C(2)-H(2)...O(1)	0.93	2.45	3.327(5)	156.1
C(7)-H(7)...O(1)	0.93	2.46	3.321(5)	154.8
C(13)-H(13)...Cl(1)	0.98	2.78	3.758(3)	173.1
C(18)-H(18)...Cl(2)#4	0.93	2.74	3.640(3)	162.6
C(32)-H(32)...Cl(3)#5	0.93	2.65	3.444(3)	143.3
Symmetry transformations used to generate equivalent atoms:				
	#1 -x+1,y,-z+1/2	#2 -x,y,-z+1/2	#3 -x+1/2,y-1/2,-z+1/2	
	#4 -x+1,-y+1,-z+1	#5 x+1/2,-y+1/2,z-1/2		

Table S6 Selected bond lengths [\AA] and angles [$^\circ$] for complex **3**

Cu(1)-N(2)	2.016(4)	N(2)-Cu(1)-N(5)	93.48(15)
Cu(1)-N(5)	2.043(3)	N(2)-Cu(1)-Cl(1)	132.98(11)
Cu(1)-Cl(1)	2.1379(16)	N(5)-Cu(1)-Cl(1)	128.97(11)

Table S7 Hydrogen bond lengths [\AA] and angles [$^\circ$] for complex **3**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(7)-H(7)...N(1)	0.93	2.41	2.948(7)	116.8
C(18)-H(18)...N(1)#2	0.93	2.44	3.276(7)	149.9
C(20)-H(20)...N(4)	0.93	2.37	2.912(7)	117.0

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y, -z+1 #2 x, y, z+1

Table S8 Selected bond lengths [Å] and angles [°] for complex **4**·2EtOH

Co(1)-N(2)	2.100(3)	Co(1)-N(1)	2.203(3)
Co(1)-N(2)#1	2.100(3)	Co(1)-Cl(1)#1	2.4161(11)
Co(1)-N(1)#1	2.203(3)	Co(1)-Cl(1)	2.4161(11)
N(2)-Co(1)-N(2)#1	82.45(17)	N(5)#1-Co(2)-N(5)	82.60(17)
N(2)-Co(1)-N(1)#1	157.66(13)	N(5)#1-Co(2)-N(4)#1	156.57(13)
N(2)#1-Co(1)-N(1)#1	75.28(12)	N(5)-Co(2)-N(4)#1	74.59(13)
N(2)-Co(1)-N(1)	75.28(12)	N(5)#1-Co(2)-N(4)	74.59(13)
N(2)#1-Co(1)-N(1)	157.66(13)	N(5)-Co(2)-N(4)	156.57(13)
N(1)#1-Co(1)-N(1)	127.03(18)	N(4)#1-Co(2)-N(4)	128.6(2)
N(2)-Co(1)-Cl(1)#1	98.81(9)	N(5)#1-Co(2)-Cl(2)	103.27(10)
N(2)#1-Co(1)-Cl(1)#1	100.98(9)	N(5)-Co(2)-Cl(2)	98.61(9)
N(1)#1-Co(1)-Cl(1)#1	84.01(9)	N(4)#1-Co(2)-Cl(2)	85.64(11)
N(1)-Co(1)-Cl(1)#1	84.30(9)	N(4)-Co(2)-Cl(2)	81.77(11)
N(2)-Co(1)-Cl(1)	100.98(9)	N(5)#1-Co(2)-Cl(2)#1	98.61(9)
N(2)#1-Co(1)-Cl(1)	98.81(9)	N(5)-Co(2)-Cl(2)#1	103.27(10)
N(1)#1-Co(1)-Cl(1)	84.30(9)	N(4)#1-Co(2)-Cl(2)#1	81.77(11)
N(1)-Co(1)-Cl(1)	84.01(9)	N(4)-Co(2)-Cl(2)#1	85.64(11)
Cl(1)#1-Co(1)-Cl(1)	153.59(6)	Cl(2)-Co(2)-Cl(2)#1	150.75(7)

Symmetry transformations used to generate equivalent atoms:

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

Table S9 Hydrogen bond lengths [Å] and angles [°] for complex **4**·2EtOH

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...Cl(2)#2	0.82	2.61	3.404(5)	165.1
C(10)-H(10)...Cl(2)	0.93	2.65	3.459(4)	146.1
C(23)-H(23)...Cl(1)	0.93	2.60	3.427(4)	148.4

Symmetry transformations used to generate equivalent atoms:

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

Table S10 Selected bond lengths [\AA] and angles [$^\circ$] for complex **5**

Zn(1)-N(2)	2.034(2)	Zn(1)-Cl(1)	2.1804(10)
Zn(1)-N(1)	2.085(2)	Zn(1)-Cl(2)	2.2080(10)
N(2)-Zn(1)-N(1)	79.71(9)	N(2)-Zn(1)-Cl(2)	111.04(7)
N(2)-Zn(1)-Cl(1)	118.56(7)	N(1)-Zn(1)-Cl(2)	110.48(7)
N(1)-Zn(1)-Cl(1)	113.78(8)	Cl(1)-Zn(1)-Cl(2)	117.33(4)

Fig. S1 30% ORTEP structure of complex **1**·2EtOH.

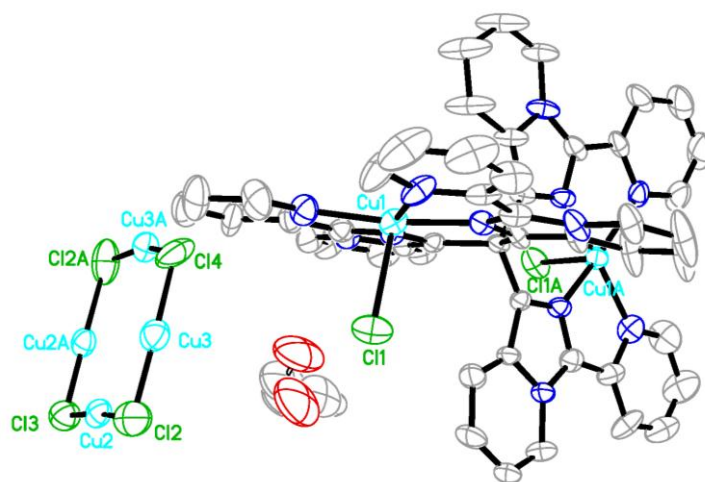


Fig. S2 Hydrogen bond structure of complex **1**·2EtOH (other hydrogen atoms of **L1** were omitted for clarity)

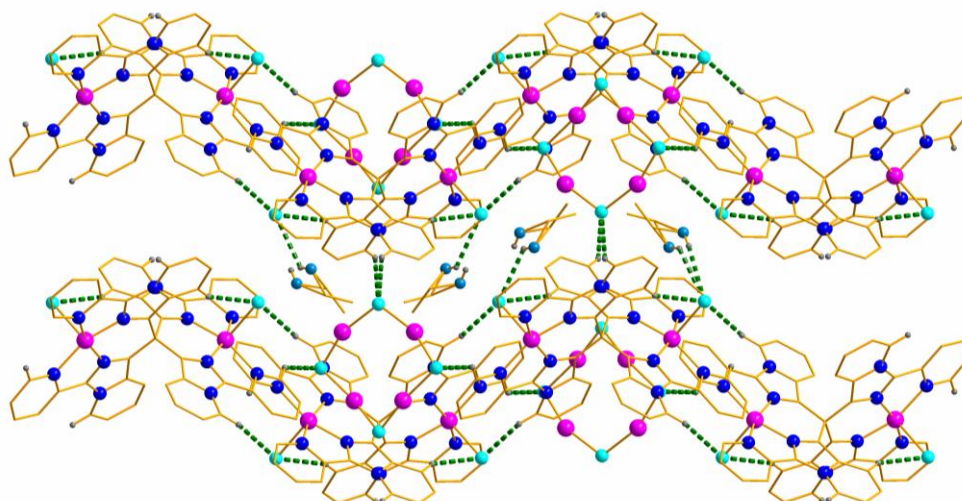


Fig. S3 IR spectrum of complex **1**·2EtOH

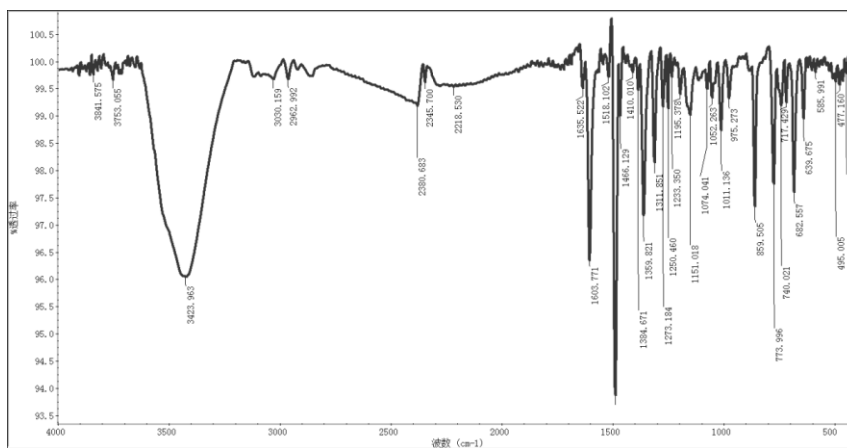


Fig. S4 30% ORTEP structure of complex **2**·2EtOH.

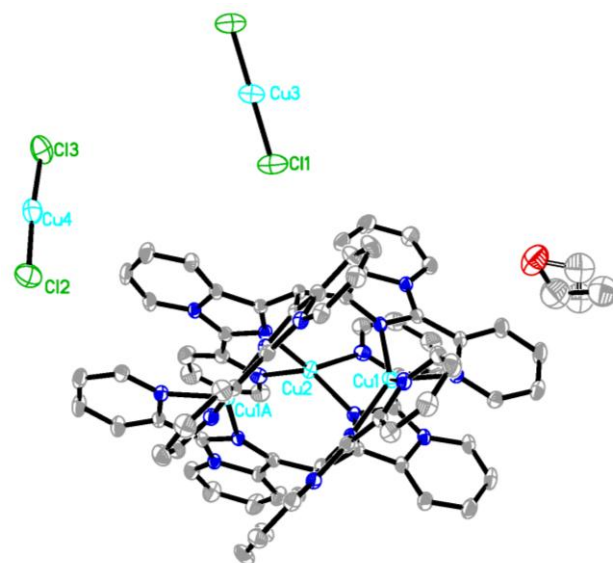


Fig. S5 IR spectrum of complex **2**·2EtOH

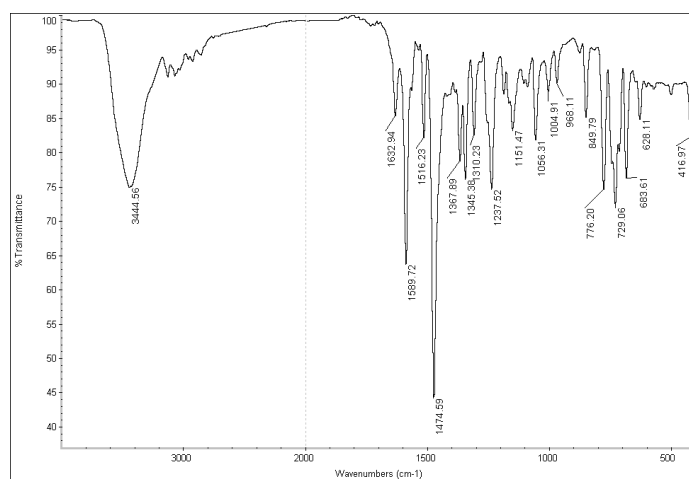


Fig. S6 IR spectrum of complex **3**

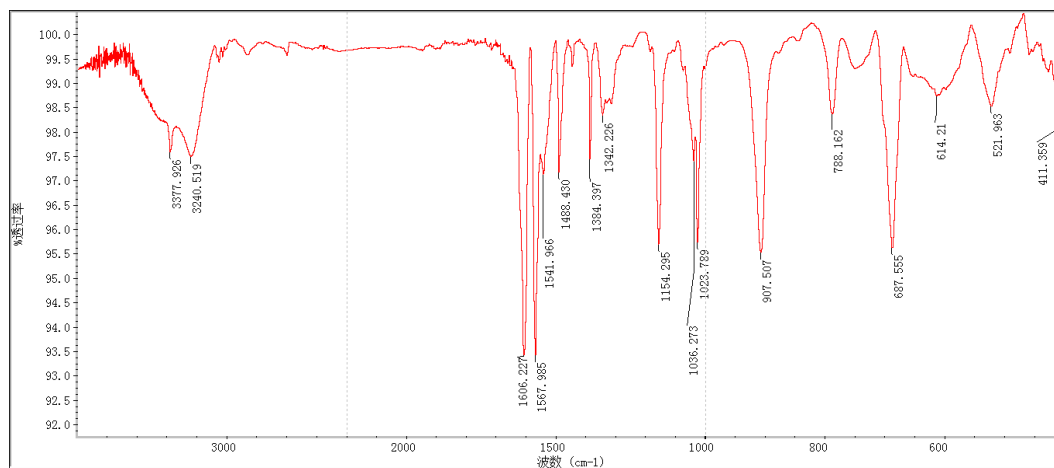


Fig. S7 30% ORTEP structure of complex **L4**

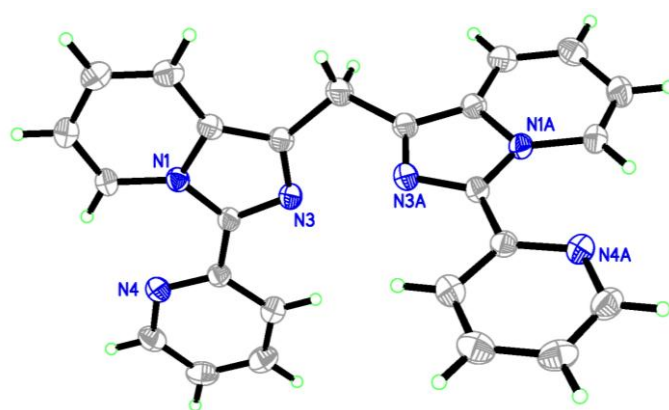


Fig. S8 IR spectrum of compound **L4**



Fig. 9 ¹H NMR spectrum of compound **L4**

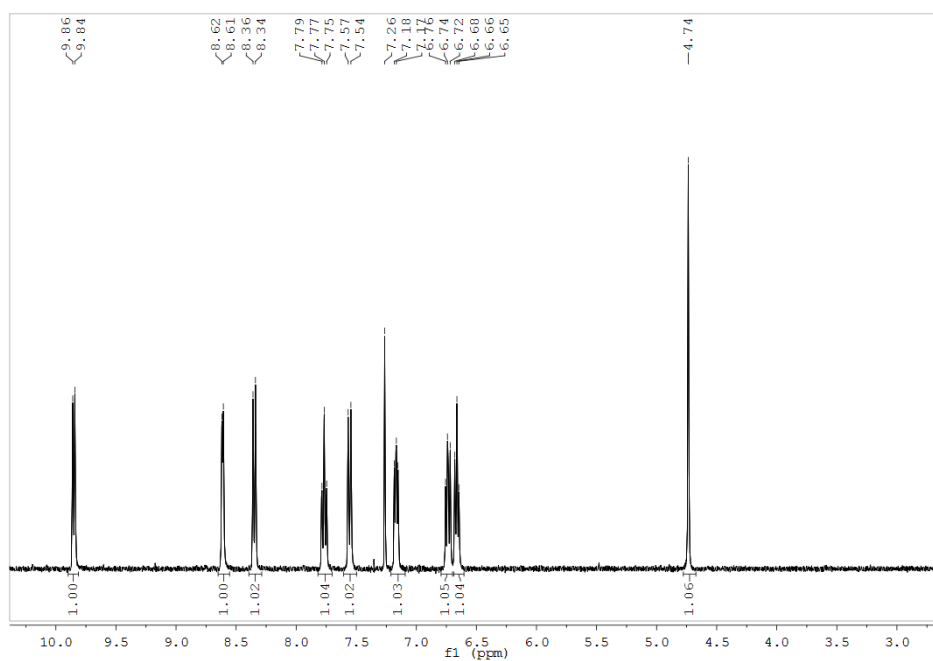


Fig. S10 30% ORTEP structure of complex **4**·2EtOH

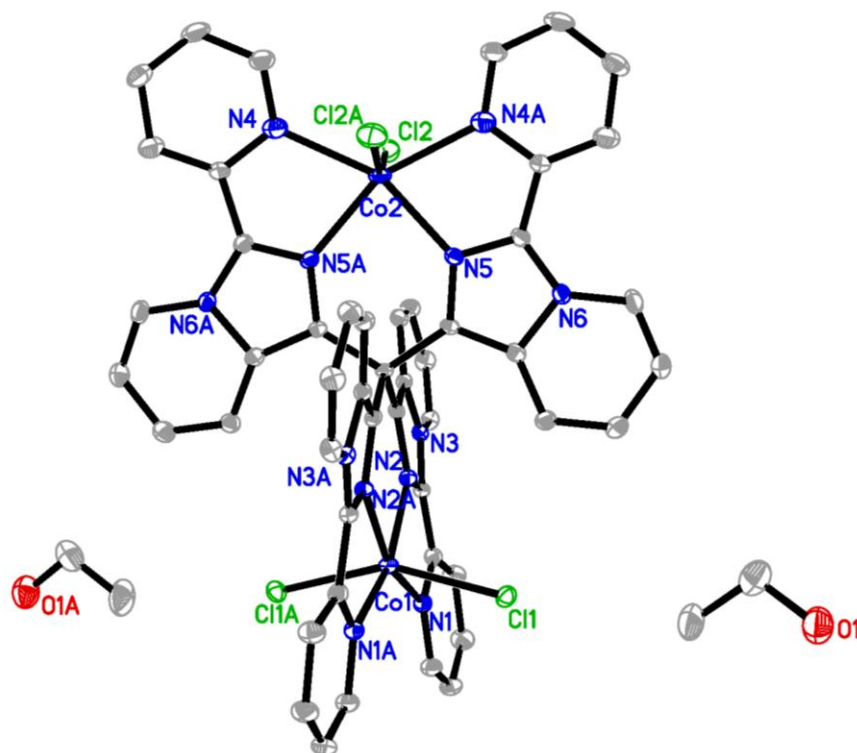


Fig. S11 Intermolecular hydrogen bond structure of complex **4**·2EtOH

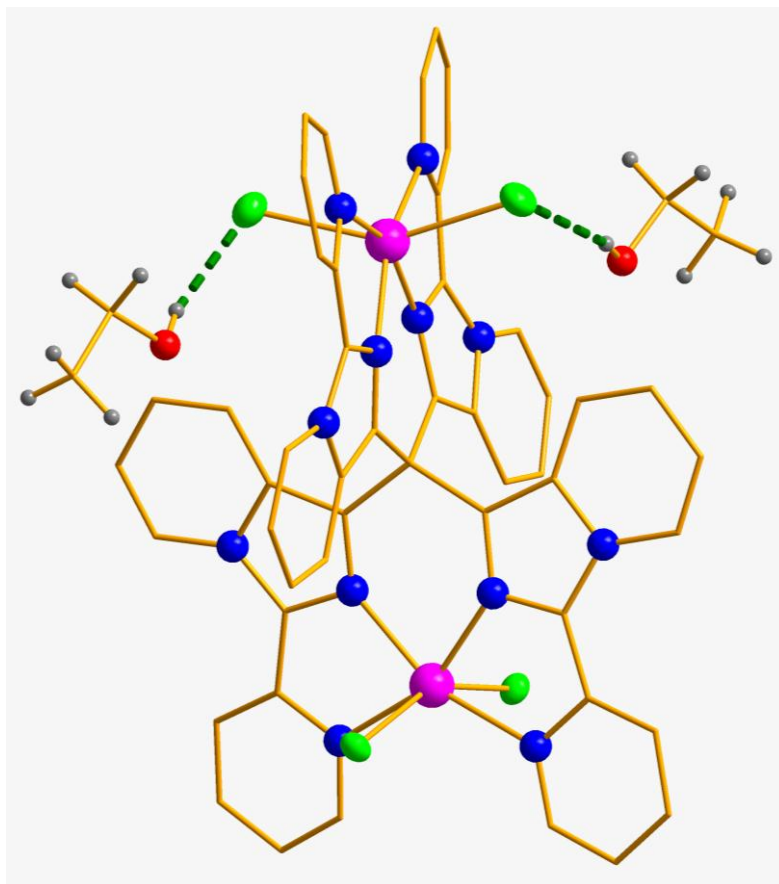


Fig. S12 The π - π stacking interactions of complex **4**·2EtOH

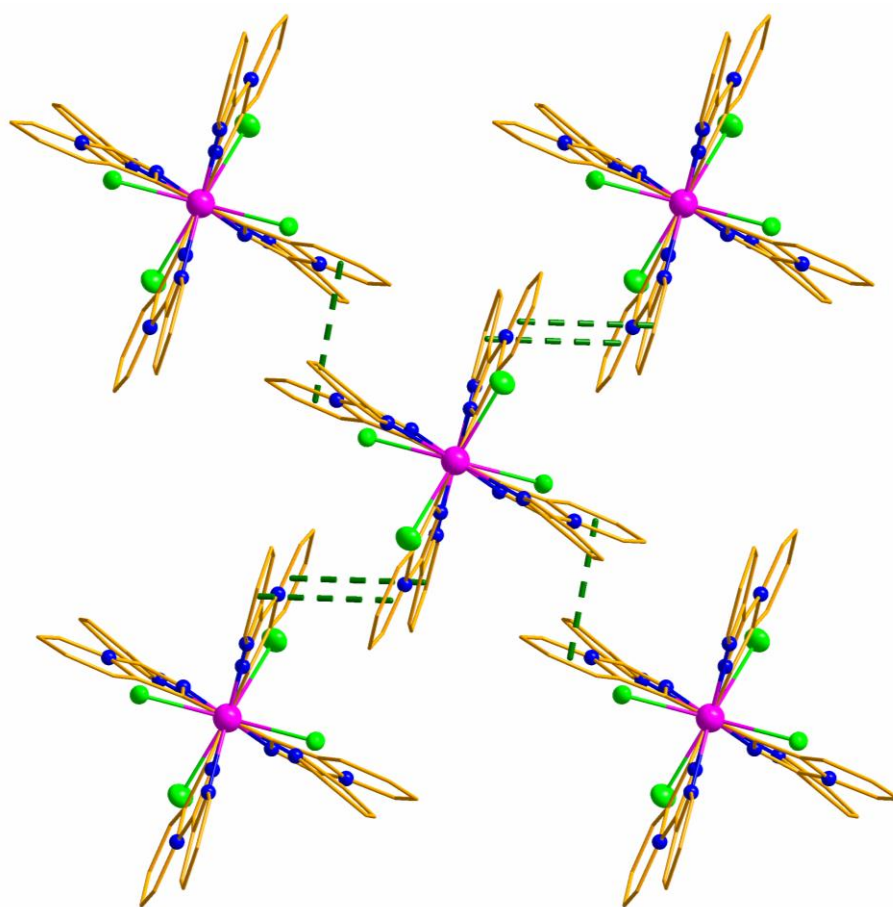


Fig. S13 IR spectrum of complex **4**·2EtOH

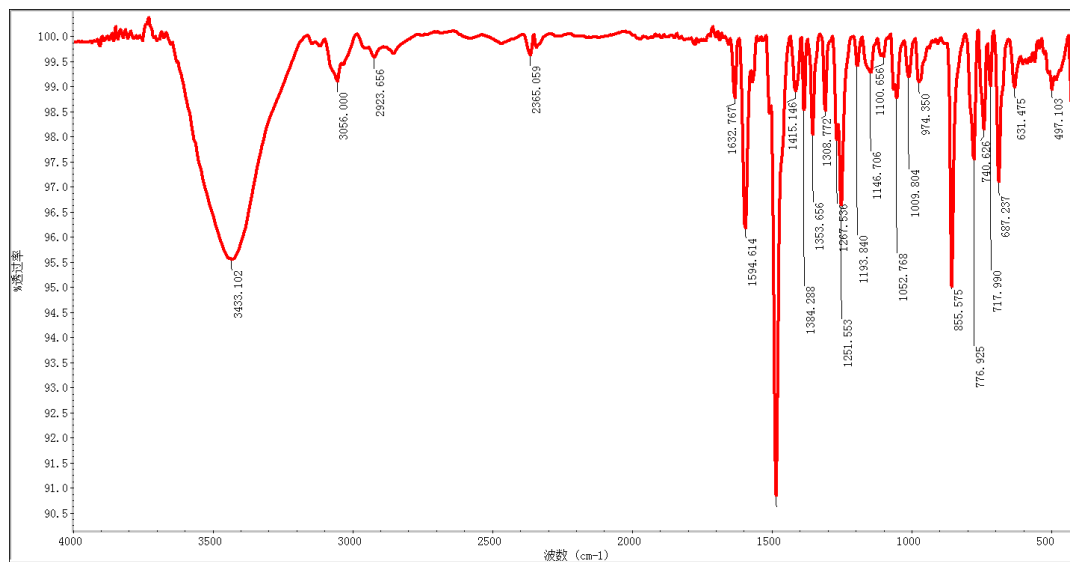


Fig. S14 30% ORTEP structure of complex **5**

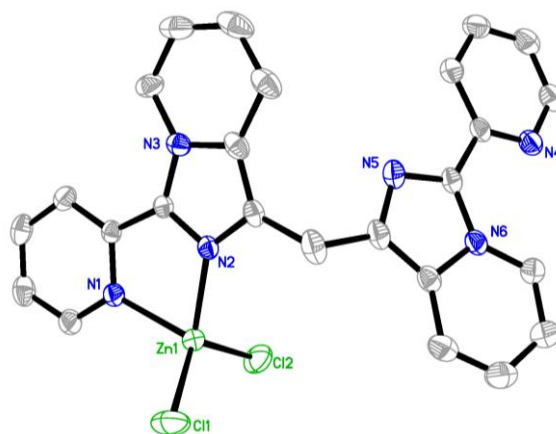
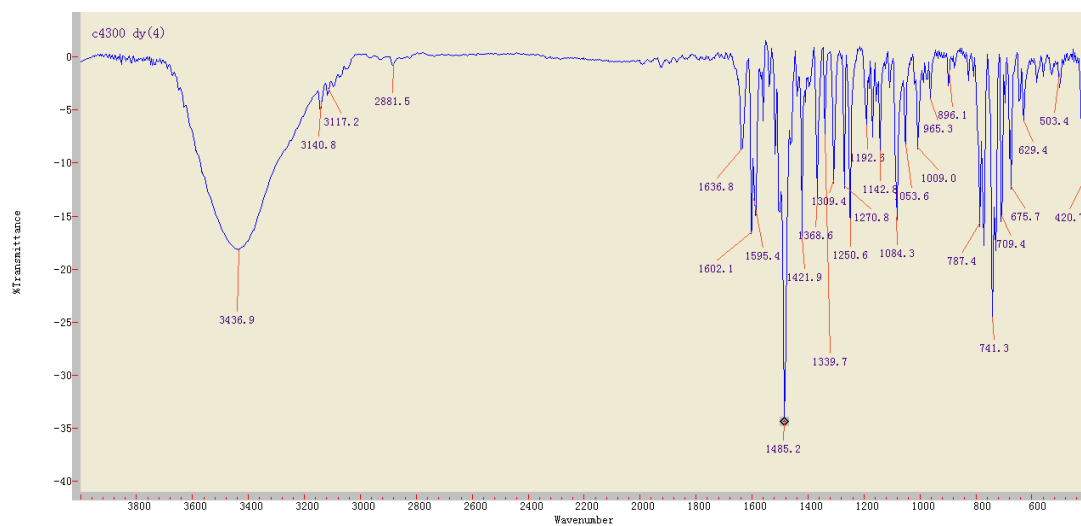
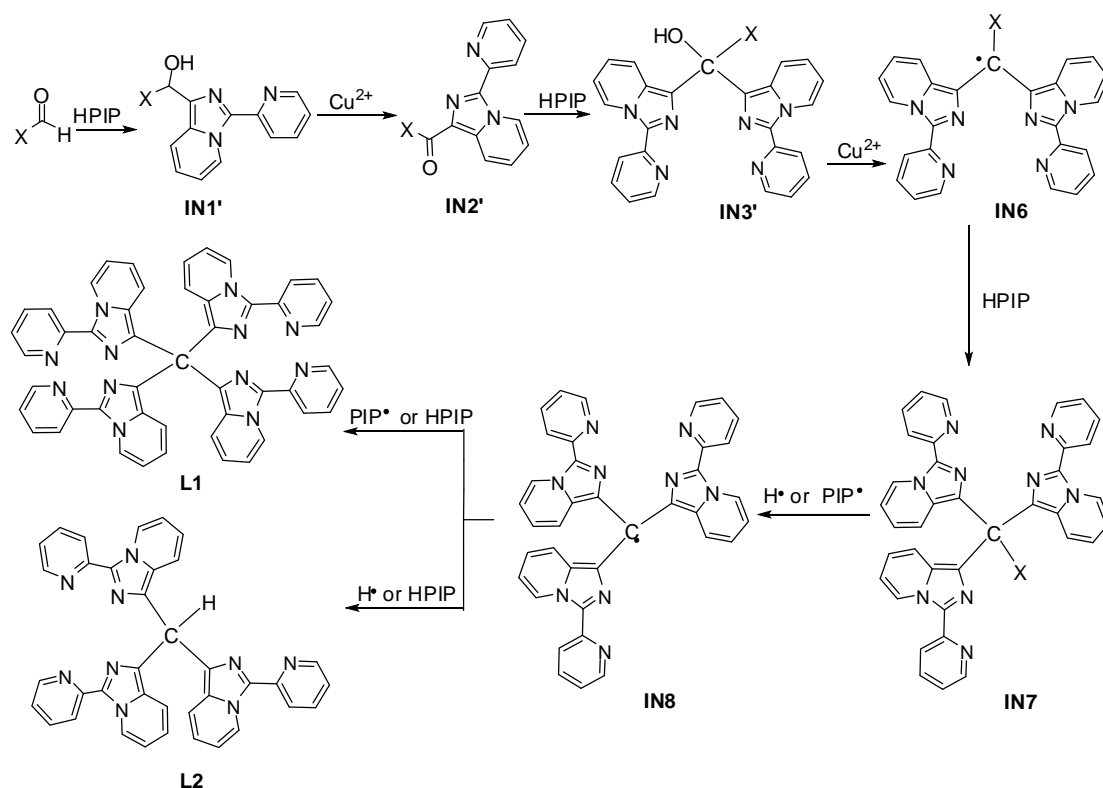


Fig. S15 IR spectrum of complex **5**



Scheme S1 The proposed radical mechanisms for the formations of the **L1-L3** ligands from formic acid, N,N-dimethyl amide and oxalaldehyde



The proposed mechanisms for the constructions of **L1** and **L2** from formic acid, N,N-dimethyl amide and oxalaldehyde are outlined in Scheme S1. Initially, the condensation reaction between HPIP and $XCHO$ ($X = OH, NMe_2, CHO$) gives an alcoholic intermediate **IN1'**, which is then oxidized by Cu^{2+} to produce **IN2'**. The subsequent condensation of **IN2'** with another equiv of HPIP generates a new alcoholic intermediate **IN3'**. Next, the cleavage of C-O bond of **IN3'** gives a radical intermediate **IN6**, which then attacks the electron-rich HPIP to afford a new compound **IN7**. The attack of the radical produced by HPIP to **IN7** produces a new radical **IN8**. Two competitive reactions may occur for **IN8**. (1) Formation of **L1** upon combining with a PIP radical or attacking HPIP. (2) **IN8** combines with a hydrogen radical or attacks one equiv of HPIP to generate **L2**.