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Hydrothermal Synthesis, Crystal Structures and Properties of Zinc(II) Di-nuclear Complex and Copper(I) Coordination Polymer Based on Building Block 2-Phenyl-4,6-di(pyridin-2-yl)pyrimidine

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A tetradentate ligand of 2-phenyl-4,6-di(pyridin-2-yl)pyrimidine (L) has been synthesized and its complexes with ZnI_2 and CuI have been obtained by hydrothermal method. single crystal X-ray diffraction analysis indicates that ligand L coordinates with Zn(II) ions to form a simple four-coordinate di-nuclear complex, while the complexation of L with Cu(I) constructs a one-dimensional chain polymer. The existence of I^- ion hampers the L to assemble grid-type complexes with Zn(II) and Cu(I). Fluorescence spectra show that the L emits blue fluorescence while its Cu(I) polymer decrease the fluorescence intensity and Zn(II) complex quenches the fluorescence.

Key Words : Pyrimidine derivative, Zinc(II) Di-nuclear complex, Copper(I) polymer, Crystal structure, Fluorescence

Introduction

The self-assembly of suitable polydentate ligands with metal ions allows the preparation of well-defined inorganic supramolecular architectures in solution. In the last few years, much effort has been focused on the generation of inorganic arrays of various types in view of their promising physico-chemical properties and their potential application in nano-technology.[1-5] Among the various arrays, there is an increasing interest in [2×2] grid-shaped complexes based on ligands containing pyrimidine-type or pyridine-type groups and various transition metal ions. These grids are thermodynamically most stable when metal ions of tetrahedral or octahedral coordination geometry are combined with a planar ligand containing polydentate binding subunits.[6-10] The [2×2] grid complexes can not only form well-defined supramolecular architectures,[11] but also exhibit interesting properties, such as special optical,[12] magnetic[13,14] and electrochemical features.[15] On the other hand, the chemistry of Zn and Cu received considerable attention in recent years due to the fact that these metal centers are catalytically active in a variety of metalloenzymes.[16-18]

Sparked by aforementioned reports, we designed and synthesized a new ligand, 2-phenyl-4,6-di(pyridin-2-yl)pyrimidine (L), which is an analogue of those ligands used to construct [2×2] grid complexes in the earlier literature.[6-9] We wanted to fabricate two new [2×2] grid complexes through this new ligand with Zn(II) and Cu(I) ions. However, two unexpected non-grid complexes were obtained when the L reacted with ZnI_2 and CuI, including a simple Zn(II) di-nuclear complex and a one-dimensional chain Cu(I) coordination polymer.

Herein, we wish to report the synthesis of the ligand and the two complexes as well as the crystal structures of Zn(II) and Cu(I) complexes. The fluorescence spectra measurements for the ligand and the complexes are also reported.

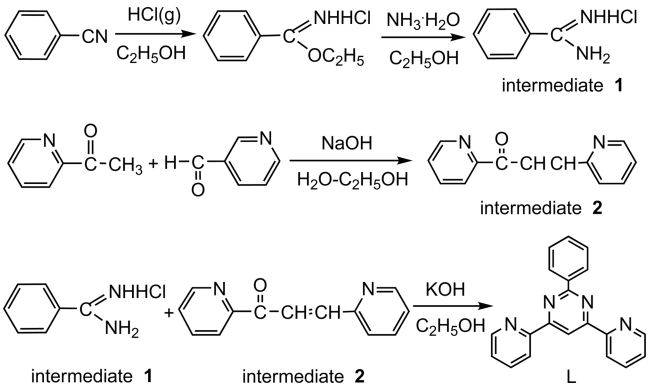
Experimental

Physical Measurements. Elemental analyses for carbon, hydrogen and nitrogen were performed by a Perkin-Elmer 240C elemental instrument. The melting points were determined on a Yanaco MP-500 melting point apparatus. IR spectra (4000-400 cm^{-1}), as KBr pellets, were recorded on a Nicolet FT-IR spectrophotometer. ^1H NMR spectra (DMSO-d_6) were recorded on Avance Mercury plus-400 instrument with TMS as an internal standard. The fluorescence spectra in DMF solvent were measured on a F96-fluorospectrophotometer.

Synthesis of Ligand L. All chemicals were obtained from a commercial source and used without further purification.

The ligand of 2-phenyl-4,6-di(pyridin-2-yl)pyrimidine (L) was synthesized by a three-step procedure (Scheme 1).

The first step was to synthesize intermediate **1.** To a 250 mL three-necked flask were added cyanobenzene (0.5 mol) and C_2H_5OH (0.6 mol) with stirring. Under −10 ~ 0 °C, HCl gas was put into reaction flask until it was saturated, giving a lot of white solid. Subsequently, at room temperature, 15% NH_3-C_2H_5OH (140 mL) solution was added into the flask and the mixture was stirred. After 24 h stirring, the mixture became to white pulp and the reaction was stopped. The mixture was filtered and the filtrate was concentrated by



Scheme 1. The synthesis of ligand L.

rotary evaporation to afford intermediate **1**. Yield: 80%. mp 82-84 °C.

The second step was to synthesize intermediate **2**. To a 250 mL three-necked flask was added a solution of NaOH (0.24 g, 6.0 mmol) in water (25 mL) and C_2H_5OH (25 mL). Nicotinaldehyde (1.98 mL, 20.8 mmol) was then added dropwise with stirring. After temperature of the reactants was controlled under 10 °C by using an ice-bath, 2-acetylpyridine (2.05 mL, 20 mmol) was added dropwise slowly. The resulting mixture was stirred for 2 h and white flocks formed. The solid was filtered out and washed three times with distilled water. Finally, the white solid was dried at room temperature to afford intermediate **2**. Yield: 85%. mp 62 °C.

The third step was to synthesize ligand L. To a 100 mL three-necked flask were added intermediate **1** (0.1 mol), intermediate **2** (0.1 mol), KOH (0.2 mol) and C_2H_5OH (30 mL). The mixture was refluxing with stirring for 3 h and then the reaction stopped. White product, ligand L, was obtained by filtration. Yield: 60%. mp 246 °C. IR (KBr pellet): 3417, 3025, 1589, 1544, 1414, 1318, 1221, 968, 832, 798, 595 cm^{-1}. Anal. Calcd. for [$C_{20}H_{16}N_4$]: C, 76.90; H, 5.16; N, 17.94. Found: C, 76.84; H, 5.20; N, 17.88%. ^1H NMR (400 MHz, DMSO) δ 9.24 (s, 1H, -H in pyrimidine ring), 8.70 (d, 2H, -H in pyridyl-ring), 7.82-7.60 (m, 4H, -H in pyridine ring), 7.46-7.20 (m, 7H, -H in pyrimidine ring and pyridine ring).

Synthesis of Zn(II) Complex. An aqueous solution (20 mL) of ZnI_2 (0.638 g, 2 mmol) was mixed with ligand L (0.624 g, 2 mmol) with stirring. The mixture was then sealed in a 50 ml stainless-steel reactor with Teflon-lined reactor at 160 °C for 4 days, resulting in the formation of light yellow crystals of the Zn(II) complex. IR (KBr pellet): 3436, 2926, 1603, 1538, 1478, 1393, 1082, 892, 757, 699, 474 cm^{-1}. Anal. Calcd. for [$C_{20}H_{14}I_4N_4Zn_2$]: C, 25.32; H, 1.49; N, 5.91. Found: C, 25.12; H, 1.34; N, 5.98%.

Synthesis of Cu(I) Complex. An aqueous solution (20 mL) of CuI (0.380 g, 2 mmol) was mixed with ligand L (0.624 g, 2 mmol) with stirring. Then the mixture was sealed in a 50 mL stainless-steel reactor with Teflon-lined reactor at 160 °C for 4 days, resulting in the formation of blue crystals of the Cu(I) complex. IR (KBr pellet): 3433, 3063, 1632, 1585, 1468, 1380, 1087, 888, 756, 609, 479 cm^{-1}. Anal. Calcd. for [$C_{20}H_{14}Cu_2I_2N_4$]: C, 34.75; H, 2.04; N, 8.11. Found: C, 34.65; H, 2.14; N, 8.22%.

Crystal Structure Determination. The single crystals of the two complexes were mounted on an Enraf-Nonius

Table 1. Summary of crystallographic results for the two complexes

Empirical formula	$C_{20}H_{14}I_4N_4Zn_2$	$C_{20}H_{14}Cu_2I_2N_4$
Formula weight	948.69	691.23
Temperature	294(2) K	293(2)
Wavelength	0.71073 Å	0.71073 Å
Crystal system,	Monoclinic	Monoclinic
Space group	*P*21/*c*	*C*2/*c*
Unit cell dimensions	a = 14.650(3) Å	a = 11.760(2) Å
	b = 12.555(3)Å	b = 14.750(3) Å
	c = 17.545(7) Å	c = 11.690(2) Å
	β =125.76 (2)°	β = 92.29(3)°
Volume	2619 (1) $Å^3$	2026.1(6) $Å^3$
Z, Calculated density	4, 2.406 Mg/m^3	4, 2.266 Mg/m^3
Absorption coefficient	6.562 mm^{-1}	5.160 mm^{-1}
F(000)	1736	1304
θ range for data collection	1.71 to 28.28°	2.22 to 28.26°
Limiting indices	$-17 \leq h \leq 19$, $-16 \leq k \leq 16$, $-23 \leq l \leq 11$	$-15 \leq h \leq 13$, $-10 \leq k \leq 19$, $-14 \leq l \leq 14$
Reflections collected / unique	16612 / 6327 [R_{int} = 0.0539]	6565 / 2438 [R_{int} = 0.0650]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6327 / 0 / 271	2438 / 0 / 129
Goodness-of-fit on F^2	1.038	0.998
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0552, wR_2 = 0.1372	R_1 = 0.0505, wR_2 = 0.0874
R indices (all data)	R_1 = 0.1014, wR_2 = 0.1596	R_1 = 0.1122, wR_2 = 0.1068
Largest diff. peak and hole	1.828 and -1.488 e. $Å^{-3}$	0.710 and -0.772 e. $Å^{-3}$

CAD4 diffractometer, respectively. Reflection data were measured at 294(2) K using graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation and a ω-2θ scan mode. The correction for *Lp* factors and empirical absorption were applied to the data. The structures were solved by direct methods and refined by full-matrix least-squares method on F_{obs}^2 using the SHELXTL software package.[19] All non-H atoms were anisotropically refined. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent C atoms. For the Zn(II) complex, the final least-square cycle gave $R = 0.0552$, $wR_2 = 0.1372$ for 3765 reflections with $I > 2\sigma(I)$ using the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0733\,P)^2 + 0.3901\,P]$, where $P = (F_o^2 + 2F_c^2)/3$. For the Cu(I) complex, the final least-square cycle gave $R = 0.0505$, $wR_2 = 0.0874$ for 1322 reflections with $I > 2\sigma(I)$ using the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0359\,P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray Crystallography.[20] The key crystallographic data are given in Table 1.

Results and Discussion

Description of the Crystal Structure of Zn(II) Complex. The displacement ellipsoid plot with the numbering scheme for the Zn(II) complex is shown in Figure 1. Figure 2 shows a perspective view of the crystal packing in the unit cell. Selected bond lengths and bond angles are listed in Table 2.

The X-ray crystal structure reveals that each ligand connects two Zn(II) ions in NˆN chelation modes to form a discrete dinuclear zinc complex (Figure 1), which crystallizes in monoclinic space group *P*21/*c*. The coordination geometry around each Zn atom is a distorted tetrahedron completed by two I atoms and two N atoms, which come from the pyridine and pyrimidine rings of ligand L, respectively. The four Zn-I bond distances are in the range of 2.510(1)-2.544(1) Å and the four Zn-N bond distances range from 2.069(7) to 2.129(6) Å. They are all consistent with those observed in a similar tetrahedral Zn complex, with Zn-I distances being from 2.514(1) to 2.526(1) Å and Zn-N distances changing from 2.023(8) to 2.103(7) Å.[21] All of the bond distances and bond angles in the ligand L are in the normal range. The pyridine ring containing N(1) atom and C(6), N(2) and C(14) atoms define a plane P1, while the other pyridine ring containing N(4) atom and C(8), N(3) and C(14) atoms define another plane P2. The dihedral angle between P1 and P2 is 9.68(2)° and the dihedral angles between the phenyl ring and the P1 and P2 are 58.31(3)° and 59.79(3)°, respectively.

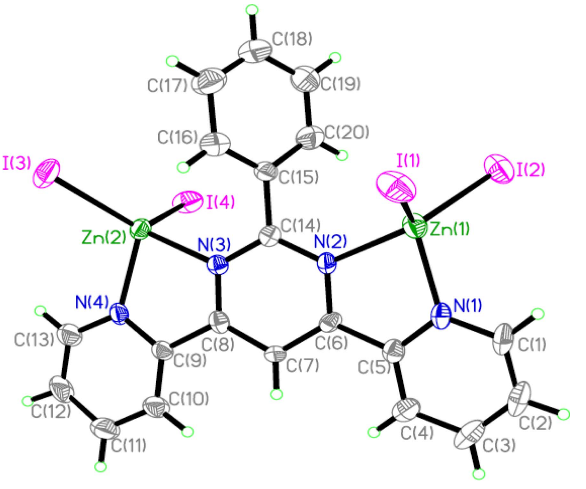


Figure 1. The molecular structure for the Zn(II) di-nuclear complex.

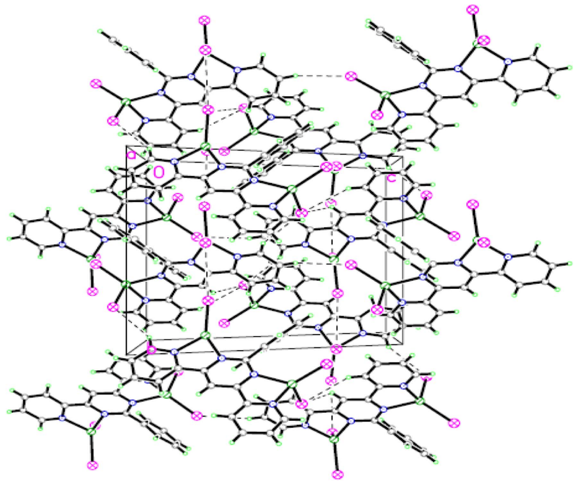


Figure 2. Packing diagram of the unit cell for the Zn(II) di-nuclear complex.

Table 2. Selected bond lengths (Å) and bond angles (°) for the Zn(II) complex

I(1)-Zn(1)	2.513 (1)	N(1)-C(1)	1.332 (1)
I(2) Zn(1)	2.541(1)	N(2)-C(6)	1.349(1)
I(3)-Zn(2)	2.510 (1)	N(3)-C(8)	1.332(1)
I(4)-Zn(2)	2.544(1)	N(4)-C(9)	1.341(1)
Zn(1)-N(1)	2.069(7)	C(4)-C(5)	1.387(1)
Zn(1)-N(2)	2.129(6)	C(5)-C(6)	1.455(1)
Zn(2)-N(4)	2.070(7)	C(12)-C(13)	1.340(1)
Zn(2)-N(3)	2.109(6)	C(15)-C(16)	1.370(1)
N(1)-Zn(1)-N(2)	78.4(2)	N(4)-Zn(2)-N(3)	79.0(2)
N(1)-Zn(1)-I(1)	114.1(2)	N(4)-Zn(2)-I(3)	110.2 (2)
N(2)-Zn(1)-I(1)	111.4(2)	N(3)-Zn(2)-I(3)	125.6(2)
N(1)-Zn(1)-I(2)	106.6 (2)	N(4)-Zn(2)-I(4)	108.3(2)
N(2)-Zn(1)-I(2)	124.7(2)	N(3)-Zn(2)-I(4)	104.4(2)
I(1)-Zn(1)-I(2)	115.3 (4)	I(3)-Zn(2)-I(4)	120.9 (5)
C(1)-N(1)-C(5)	119.4(8)	C(7)-C(6)-C(5)	121.9(7)
C(6)-N(2)-C(14)	119.2(6)	C(12)-C(13)-N(4)	122.8(9)
C(8)-N(3)-C(14)	119.9(6)	C(16)-C(15)-C(20)	119.5(9)
C(9)-N(4)-C(13)	117.4(7)	N(2)-C(6)-C(7)	120.6(6)

Description of the Crystal Structure of Cu(I) Complex. The displacement ellipsoid plot with the numbering scheme for the Cu(I) complex is shown in Figure 3. Figure 4 shows a perspective view of the crystal packing in the unit cell. Selected bond lengths and bond angles are listed in Table 3.

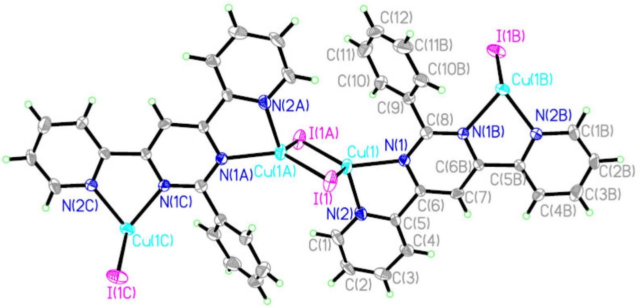


Figure 3. The molecular structure for the Cu(I) complex.

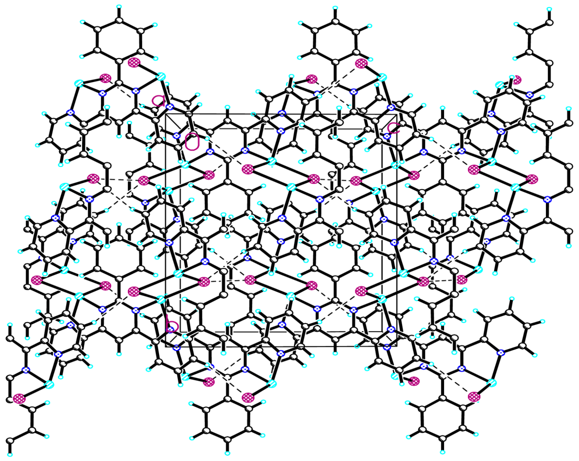


Figure 4. Packing diagram of the unit cell for the Cu(I) complex.

The crystal structure analysis indicates that the repeat unit of the Cu(I) complex contains two copper(I) atoms, one ligand (L) and two iodide ions. In each unit, there exists a *C*2 symmetry axis along the C-C bond which connects the phenyl ring and the pyrimidinyl ring together. Each Cu(I) ion adopts a distorted tetrahedral geometry and coordinates with two individual I^- ions and two N atoms, which come from the pyridyl and pyrimidinyl rings of the L, respectively. The two individual I^- ions act as two bridges to join two Cu(I) atoms to form a planar rhombic $Cu_2(\mu\text{-}I)_2$ core with bond angle Cu(1)-I(1)-Cu(1A) being 59.79(4)°. These $Cu_2(\mu\text{-}I)_2$ core units are then linked by the ligands to generate a one-dimensional coordination polymer, as shown in Figure 5. The lengths of Cu-N and Cu-I bonds are all comparable with those reported in similar complexes.[22,23] All the bond distances in the ligand L fall within the normal range. The Cu···Cu separation of 2.585(2) Å lies within the range of "cuprophilic" interactions and is comparable to that in similar iodide complexes (2.530-2.612).[22,24] The pyrimidinyl ring and two pyridyl rings are almost co-planar in P1. The dihedral angle between P1 and the phenyl ring is 49.77(3)°.

Table 3. Selected bond lengths (Å) and bond angles (°) for the Cu(I) complex

I(1)-Cu(1)	2.587 (1)	N(2)-C(5)	1.329(7)
I(1)-Cu(1)#1	2.600 (1)	N(2)-C(1)	1.343(8)
Cu(1)-N(2)	2.068(5)	C(1)-C(2)	1.344(9)
Cu(1)-N(1)	2.136(5)	C(5)-C(6)	1.499(8)
Cu(1)-Cu(1)#1	2.585(2)	C(6)-C(7)	1.372(7)
Cu(1)-I(1A)	2.600(1)	C(8)-C(9)	1.481(1)
N(1)-C(8)	1.331(6)	C(9)-C(10)#2	1.379(8)
N(1)-C(6)	1.352(7)	C(9)-C(10)	1.379(9)
Cu(1)-I(1)-Cu(1)#1	59.8(4)	C(5)-N(2)-C(1)	117.7(6)
N(2)-Cu(1)-N(1)	78.2(2)	N(2)-C(1)-C(2)	123.2(7)
N(2)-Cu(1)-I(1)	109.9(2)	N(2)-C(5)-C(6)	114.1(5)
N(1)-Cu(1)-I(1)	109.4(2)	N(1)-C(6)-C(7)	120.8(6)
N(2)-Cu(1)-I(1)#1	102.9(2)	N(1)-C(6)-C(5)	116.8(5)
N(1)-Cu(1)-I(1)#1	125.6(2)	N(1)#2-C(8)-N(1)	125.2(8)
I(1)-Cu(1)-I(1)#1	120.2(4)	C(10) #2-C(9)-C(10)	118.4(9)
C(8)-N(1)-C(6)	117.3(5)	C(10)-C(9)-C(8)	120.8(5)

Symmetry transformations used to generate equivalent atoms: #1: $-x + 1/2, -y + 1/2, -z$; #2: $-x + 1, y, -z + 1/2$

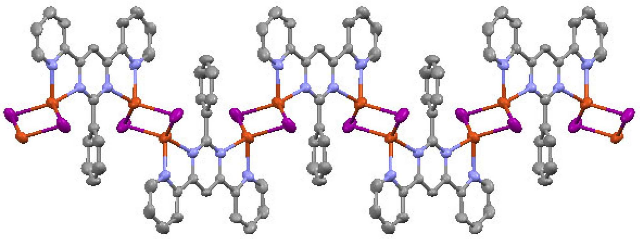


Figure 5. One-dimensional chain of the Cu(I) polymer down along the *c* axis.

Preparation of the Zn(II) and Cu(I) Complexes. Comparing the synthetic conditions of the above Zn(II) and Cu(I) complexes with those used in the earlier [2×2] grid complexes,[6-9] we found that in order to obtain [2×2] grid complexes, one must not only select the appropriate ligand, but also choose the right metal-salt. In the earlier literature, the metal-salts were not simple ones, including $[Cu(CH_3CN)_4]PF_6$, $Cu(CF_3SO_3)_2{\cdot}C_6H_6$, $Zn(BF_4)_2$, $AgCF_3SO_3$, $AgBF_4$, $Co(BF_4)_2$, Fe(BF4)2, $Mn(ClO_4)_2$ and so on. In these metal-salts, the anions are not simple anions and all these anions were found not to coordinate with metal ions in the corresponding [2×2] grid complexes. For example, Lehn and co-workers[6] ever reported a similar ligand, 2-phenyl-4,6-di(6-methyl-pyridin-2-yl) pyrimidine (Me-L), which only has one more methyl-group than the ligand L. When the Me-L reacted with $AgCF_3SO_3$, $[Cu(CH_3CN)_4]PF_6$ and $Zn(CF_3SO_3)_2$, respectively, three [2×2] grid-type coordination scaffolds with Cu(I), Ag(I) and Zn(II) were obtained and all the anions did not take part in coordination. However, in our synthesis no [2×2] grid-type complexes were formed when the L reacted with ZnI_2 and CuI, and the I^- anion acts as coligands to participate into coordination with the central metal ions. It can be deduced that the existence of I^- ions hamper the L to assemble grid-type complexes with Zn(II) and Cu(I). Similar phenomena were also reported in literature,[21] where two ligands containing pyrimidinyl groups were potential polydentate ligands to form [2×2] grid-type complexes. However, only dinuclear Cd(II) and Zn(II) complexes were found when these two ligands reacted with CdI_2 and ZnI_2, and I^- ions attached to the central metal ions, respectively.

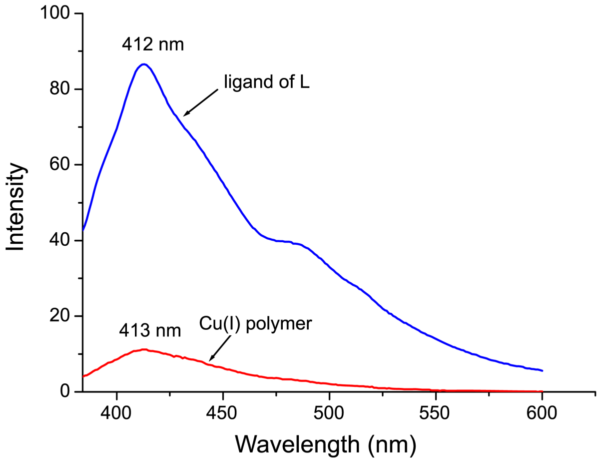


Figure 6. Fluorescence spectra for the L and the Cu(I) polymer in DMF solvent.

Fluorescence Spectra. The fluorescence spectra in DMF solvent show that ligand L exhibits an intense blue fluorescence at about 412 nm when irradiated at 365 nm, while the Cu(I) polymer displays a decreasing emission at about 413 nm (Figure 6). However, the Zn(II) di-nuclear complex quenches fluorescence completely. Generally, quenching of the fluorescence of a ligand by transition metal ions is a rather common phenomenon which involves magnetic perturbation, redox activity, electronic energy transfer, photo induced electron transfer (PET), *etc*. This is because of the facts that complexation with the metal ions increases the chance of an intraligand fluorescence quenching (PET) process and that the chelation brings in rigidity, increasing the chance of radiationless decay.[25] Namely, the chelation enhancement of the quenching (CHEQ) leads to a strong decrease in the emission intensity.[26] As for the two title complexes, just as described in the structure description section, the chelation of metal ions with the L makes the dihedral angles between the phenyl ring and the other parts of the L (pyrimidinyl ring and two pyridyl rings) being 49.77(3)° in the Cu(I) polymer and 58.31(3)°-59.79(3)° in the Zn(II) di-nuclear complex, which maybe ultimately result in their different fluorescence behaviors.

Conclusion

A ligand, 2-phenyl-4,6-di(pyridin-2-yl)pyrimidine (L), has been synthesized, which fits to construct [2×2] grid-shaped complexes. However, when the L hydrothermally reacted with ZnI_2 and CuI, a Zn(II) di-nuclear complex with the two Zn(II) ions adopting distorted tetrahedral geometry and a Cu(I) coordination polymer were obtained. In the Cu(I) polymer, each Cu(I) ion falls in tetrahedral environment and two I^- ions bridge two Cu(I) ions to form a $Cu_2(\text{-}I)_2$ core. These $Cu_2(\mu\text{-}I)_2$ core units are further linked by the ligands to generate a one-dimensional coordination polymer. Comparative studies indicate that in order to obtain [2×2] grid-shaped complexes, it is necessary to choose right metal-salts as well as organic ligands. Fluorescence spectra suggest that the L emits blue fluorescence, while its Cu(I) polymer decreases the fluorescence intensity and Zn(II) complex quenches the fluorescence.

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Supplementary Materials. Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC- 940134 for the Zn(II) complex and CCDC-94133 for the Cu(I) polymer).

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