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A series of temperature-dependent Cd^{II}-complexes containing an important family of N-rich heterocycles from in situ conversion of pyridine-type Schiff base

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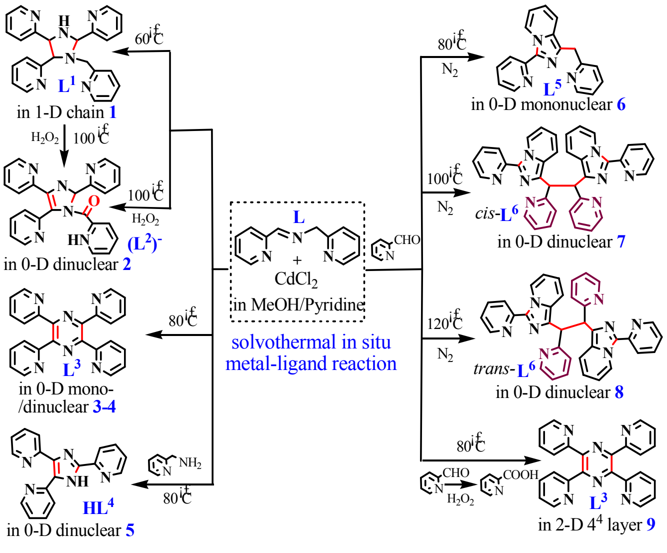
An efficient method for syntheses of a wide variety of N-rich heterocycles has been systematically explored. The synthetic protocol involves a solvothermal in situ metal-ligand reactions of pyridine-type Schiff base N-(2-pyridylmethyl)-pyridine-2-carbaldimine (**L**) with Cd^{2+} ions, resulting in the efficiently formation of nine temperature-dependent Cd^{II}-complexes **1-9** supported by six types of N-rich heterocycles $\mathbf{L^{1\text{-}6}}$. To the best of our knowledge, both the synthetic strategies with solvothermal in situ Cd^{II}-mediated Schiff base-conversion and N-rich heterocycle rings $\mathbf{L^{1\text{-}2}}$ as well as *cis*-$\mathbf{L^6}$ are firstly reported. Meanwhile, in situ formation mechanisms of $\mathbf{L^{1\text{-}6}}$ are also plausibly proposed.

Introcduction

Polyazaheteroaromatic compounds such as inmidazo[1,5-a]-pyridine, pyrazine, piperazine, imidazolidine and imidazole, as well as their derivatives are well-known for the importance in industry and are widely used as ligands in the neutral and anionic forms in organic and organometallic chemistry.[1] Usually, the preparation of these organic nitrogen-containing heterocycles involves the formation of C-C and C-N bonds mediated by transition metals. It has been well documented that most stoichiometric and catalytic C-C and C-N bond-forming reactions mediated by the middle and late transition metals typically follow oxidative addition, transmetalation and reductive elimination pathways,[2] which can assemble different kinds of aza-heterocycles in the cumbersome steps. Obviously, these traditional synthetic methods are hard to avoid, especially for nitrogen-rich complicated heterocycles, the unfavorable factors such as multi-steps, difficult purification and separation as well as low yield, etc.

On the other hand, the recently developed solvothermal in situ metal-ligand reaction[3] might be an overwhelming strategy for preparation of the complicated aza-heterocycles as well as the expected metal-complexes simultaneously. For example, some substituted derivatives of inmidazo[1,5-a]pyridine, pyrazine and piperazine were efficiently synthesized from simple starting materials catalyzed by Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ti^{4+} ions,[4] though sometimes resulting products may be the mixtures to purify difficultly. By contrast, only one example involved *tetra*-substituted imidazolidine/tri-substituted imidazole rings was reported up to now, namely Musie et al. recently found that Cu(II)-promoted imidazolidine ring was formed from Schiff base ligand of pyridine-2-imine benzoate in alkaline environment.[5]

Accordingly, it is very meaningful for systematically exploring the formation conditions and coordination chemistry of asymmetric *tetra*-substituted imidazolidine/pyrizine and symmetric inmidazo-



Scheme **1**. Construction strategies of nine Cd^{II} complexes **1-9** containing six ligands $\mathbf{L^1}$-$\mathbf{L^6}$ from in situ conversion of pyridine-type Schiff base N-(2-pyridylmethyl)pyridine-2-carbaldimine (**L**).

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[1,5-a]pyridine/tri-substituted imidazole by solvothermal in situ metal-catalyzed reaction of simple Schiff base. More interesting is the ecologically compatible synthesis of new heterocyclic compounds that are not easily accessible and that can be applied as pharmaceuticals or as ligands for the development of new catalysts and advanced luminescent/biological functional materials.[6]

Based on the above considerations, a series of complicated aza-heterocycles, such as 2,2',2''-(1-(pyridin-2-ylmethyl)imidazoli-dine-2,4,5-triyl)tripyridine (**L**^{1}), pyridin-2-yl(2,4,5-tri(pyridin-2-yl)-1,2-dihydroimidazol-3-yl)methanone (H**L**^{2}), 2,3,5,6-tetra-(pyridin-2-yl)pyrazine (**L**^{3}), 2,2',2''-(1*H* -imidazole-2,4,5-triyl)-tripyrid-ine (H**L**^{4}), 1-pyridineimidazo-[1,5-*a*]-pyridine (**L**^{5}) and 1-(1,2-di(pyridin-2-yl)-2-(3-(pyridin-2-yl)*H*-imidazo[1,5-*a*]pyrid-in-1-yl)-ethyl)-3-(pyridin-2-yl)*H*-imid-azo[1,5-*a*]pyridine (*cis*/*trans*-**L**^{6}) were prepared by cadmium-catalyzed solvothermal in situ formation from pyridine-type Schiff base of N-(2-pyridyl-methyl)pyridine-2-carbaldimine (**L**). Here, we describe the syntheses and coordination chemistry of these six N-rich heterobicycles **L**$^{1-6}$ by Cd^{II}-catalytic ring closure starting from the Schiff base **L** (Scheme **1**). Meanwhile, in situ formation mechanisms of **L**$^{1-6}$ are also plausibly proposed. To the best of our knowledge, both the synthetic strategies with solvothermal in situ Cd^{II}-mediated Schiff base-conversion and ligands **L**$^{1-2}$ as well as *cis*-**L**^{6} are reported at the first time.

Results and discussion

Synthesis

The pyridine-type Schiff base **L** was prepared readily from the condensation of equivalent 2-pyridine formaldehyde and 2-pyridylethylamine. A series of reactions catalyzed by cadmium(II) from **L** were performed in situ as shown in Scheme **1**, finally pale-yellow/reddish Cd^{II}-compounds **1**-**9** were obtained under different temperatures for three days, in which temperature factor is essential for Cd-complexes and in situ formed aza-heterocycles, mainly deriving from these cycloaddition reactions in present cases being subject to the tune of reaction temperature.

Structure and formation mechanism of Complexes 1-4

When the reaction of ligand **L** with an equimolar amount of $CdCl_2$ at less than 60°C for three days, 1-D compound $[(Cd_6(\mathbf{L}^1)_2Cl_{13})$-$(Cd(\mathbf{L}^1)Cl)]_n \cdot 2H_2O$ (**1**) was given. In the presence of H_2O_2, however, 0-D binuclear compound $[Cd(\mathbf{L}^2)Cl]_2$ (**2**) with the carbonyl group in ligand H**L**^{2} was obtained. The crystal structure of the pale yellow block compound **1** is shown in Figure **1**, exhibiting a 1-D zigzag-chain structure. The asymmetric unit of **1** consists of one six nuclear anion $[Cd_6Cl_{13}(\mathbf{L}^1)_2]^-$ unit (Figure **1a**) and one cation $[Cd\mathbf{L}^1Cl]^+$ unit (Figure **1c**), and two water molecules. In the anionic part, six Cd^{II} ions present three kinds of coordination modes, namely, tetrahedral geometry for Cd6 atom supported by four chloride ions (one μ_2-Cl10, and three terminal Cl11, Cl12, Cl13), the distorted square pyramid for Cd4 atom surrounded by three chloride ions (two μ_2-Cl7/Cl9, and one terminal Cl8) and two nitrogen atoms (N10, N11) from the same ligand **L**^{1}. The distorted octahedral geometries for four Cd1, Cd2, Cd3 and Cd5 atoms, in which Cd1 was surrounded by two μ_2-Cl1/Cl2 ions and four nitrogen atoms (N1, N2, N3 and N6) from the same ligand **L**^{1}, Cd2 by six μ_2-Cl ions (Cl1, Cl2, Cl3, Cl5, Cl6, Cl7), Cd3 by two chloride ions (one μ_2-Cl3, one terminal Cl4) and four nitrogen atoms (N7, N8, N9 and N12) from the same ligand **L**^{1}, and Cd5 by four μ_2-Cl ions (Cl5, Cl6, Cl9 and Cl10) and two nitrogen atoms (N4 and N5) from the same ligand **L**^{1}. Six adjacent Cd^{II} atoms were connected into Cd_6Cl_{13} unit through single or double μ_2-bridging Cl atom (Figure **S1**), which was further linked into 1D wave-like anionic chain (**1**) (Figure **1d-e**) with the smallest repeating unit $[Cd_6Cl_{13}(\mathbf{L}^1)_2]^-$ moiety via μ_2-η^1:η^1:η^1:η^1:η^1:η^1 coordination mode of ligand **L**^{1} (Figure **1b** and **1e**). On the other hand, the Cd7 atom in each cationic unit is hexa-coordinated by one terminal chloride atom (Cl14) and five nitrogen atoms from the same ligand **L**^{1} (N13, N14, N15, N17, N18) with μ_1-η^1:η^1:η^1:η^1:η^1 coordination mode to form a $[Cd\mathbf{L}^1Cl]^+$ unit presenting distorted octahedral geometry (Figure **1c**). All Cd-Cl and Cd-N bond distances are from 2.839(4) to 2.883(4) and 2.439(4) to 2.483(4) Å, respectively (Table **S2**), which are similar to those reported.[7]

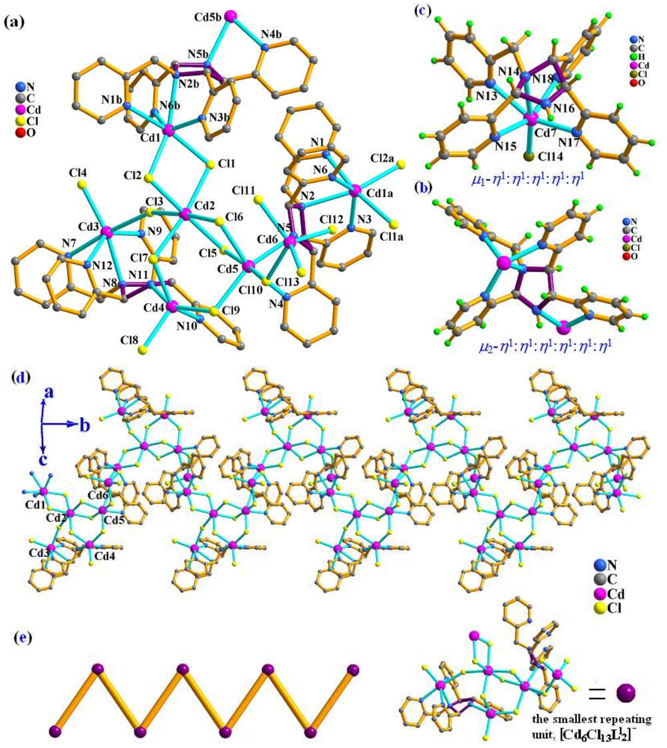


Figure **1**. In **1**, (a)-(b) the coordination environment of six Cd^{2+} ions and coordination mode of ligand **L**^{1} in anionic part. (c) the structure of cationic moiety and another coordination mode of ligand **L**^{1}. (d)-(e) 1-D wave-like anionic chain with the smallest unit $[Cd_6Cl_{13}(L^1)_2]$ along *b* axis. The symmetric codes: a) 1-x,0.5+y,0.5-z; b) 1-x,-0.5-y,0.5-z.

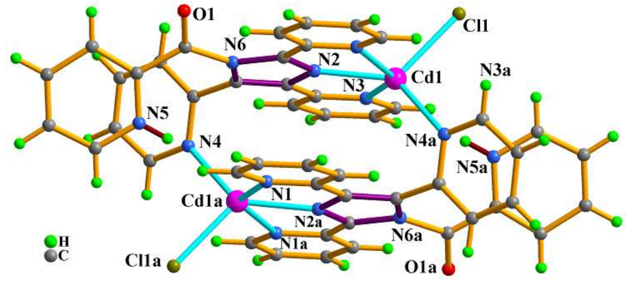


Figure **2**. Molecular structure of **2** with partial atomic labels, and two uncoordinated methanol molecules are omitted for clarity. The symmetric code: a) 1-x,2-y,1-z.

Compound **2** is a 0-D dinuclear structure with the asymmetric unit consisting of one crystallographically unique Cd^{II} atom, one coordinated chloride ion, one (L^2)$^-$ ligand and one uncoordinated methanol molecule as shown in Figure **2**. Different from those in **1**, Cd^{II} atom in **2** is only penta-coordinated in a distorted square pyramid with N4Cl donor set, in which coordination sphere around Cd1 consists of one terminal Cl atom and three pyridyl N atoms (N1, N3, N4a) from the same ligand (L^2)$^-$, one imidazolium N atom (N2) from another ligand (L^2)$^-$. Compared with ligand L^1 in **1**, ligand HL^2 in **2** may derive from oxidation of the methylene on L^1 into carbonyl group and the dehydrogenation of imidazolidine core ring into delocanized imidazolium ring, accompanied by the protonation of the pyridine nitrogen atom (Scheme **2**). Therefore, ligand (L^2)$^-$ in **2** shows μ_2-η^1:η^1:η^1:η^1:η^1 coordination mode, further forming dinuclear compound **2** with similar bond distances of Cd-N (2.160(5) to 2.572(5) Å). Similar to complex **1**, 3-D supramolecular network of **2** constructed by hydrogen bonds C-H···Cl(O) is shown in Figure **S2**.

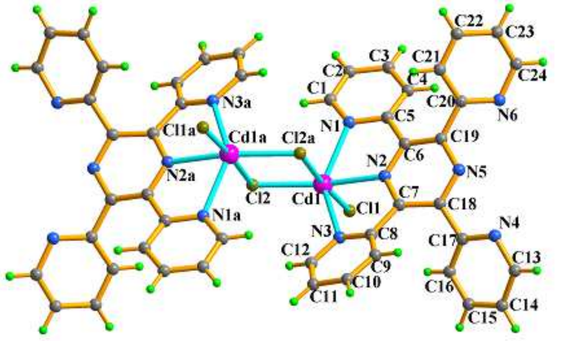


Figure **3**. Molecular structure of **3** with partial atomic labels, and the symmetric code: a) 1-x,1-y,2-z.

When the reaction of ligand **L** with an equimolar amount of CdCl$_2$ at more than 70°C for three days, two 0-D compounds [Cd(**L^3**)Cl$_2$]$_2$ (**3**) (at 80°C) and Cd$_2$(**L^3**)Cl$_4$·H$_2$O (**4**) (at 100°C) involving pyrizine-core **L^3** ligand were given, respectively. The crystal structure of the pale yellow block compound **3** is shown in Figure **3**, exhibiting a 0-D binuclear structure. The asymmetric unit of **3** involves one Cd^{2+} ion, one in situ formed L^3 ligand, and two Cl$^-$ ions. The coordination geometry around Cd1 is octahedral with three nitrogen N atoms (N1, N2, N3) from one L^3 ligand and three chlorine atoms (Cl1, Cl2, Cl2a), in which Cl2, N1, N2, N3 atoms occupy the corners of a square, and Cl1 and Cl2a atoms at the apical positions. The ligand L^3 in **3** has the same coordination mode **I:** μ_1-η^1:η^1:η^1, namely, which as a terminal tridentate ligand using the three nitrogen atoms (N1, N2, N3) on the same side of L^3 coordinates to one Cd^{2+} ion to form a 0-D dinuclear structure via two μ_2-bridging Cl2 atoms. The Cd-N and Cd-Cl bond distances are 2.345(8)-2.370(7) Å and 2.470(3)-2.863(3) Å, respectively. And intermolecular hydrogen bonding C-H···Cl interaction resulting in 1-D supramolecular chain further stabilizes crystal structure (Figure **S3** and Table **S3**).

The pale yellow prism complex **4** is crystallized in a monoclinic space group *C*2/*c* with two Cd^{II} atoms, four chlorine atoms, one ligand L^3, and one crystallization water molecule in one molecule as depicted in Figure **4**. The cadmium center is penta-coordinated to three nitrogen atoms (N1, N2, N3) from the same L^3 and two terminal chlorine atoms (Cl1, Cl2) in a slightly distorted triganol bipyrimidal geometry with the normal Cd-N(Cl) bond distances and comparable to previously reported metric data for similar complexes. The ligand L^3 in **4** adopts another coordination mode **II**: μ_2-η^1:η^1:η^1:η^1:η^1:η^1 to bridge two CdCl$_2$ units and generates a dinuclear compound **4**. Considering weak interaction of Cl2 atom to Cd1 center with Cl2···Cd1 separation of 3.15 Å, 1-D chain displayed in Figure **S4** is formed in *ac* plane. Meanwhile, some interchain hydrogen bonding C-H···Cl interactions contribute to stability of packing structure (Figure **S5** and Table **S3**).

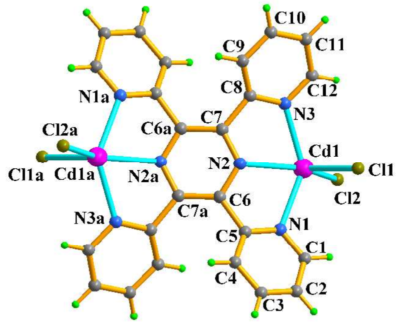
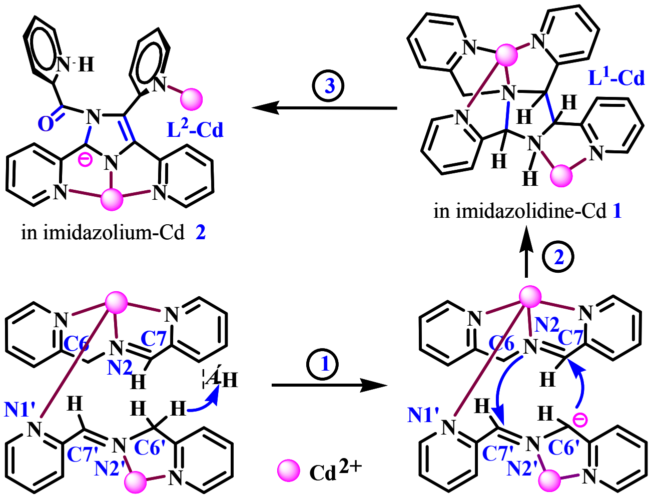


Figure **4**.Molecular structure of **4** with partial atomic labels, and lattice water molecule is omitted for clarity. The symmetric code: a) 0.5-x,0.5-y,1-z.

From above analyses and Scheme **1**, ligand L^1 in compound **1** has imidazolidine-core ring with three 2-pyridyl substituents in 2,4,5-positions and one pyridin-2-yl-methyl group in 3-position. Different from L^1, ligand (L^2)$^-$ in **2** contains planar imidazolium-core ring and its 3-position connects one 2-pyridyl group via carbonyl group. Both compounds **3** and **4** contain ligand L^3, which is pyrazine-core ring with four 2-pyridyl substituents in 2,3,5,6-positions (Scheme **1**). Three ligands **L$^{1-3}$** can be successfully isolated from the reactions of those compounds containing corresponding ligands with Na$_2$S. Obviously, Schiff base **L** in the assembly process of four compounds **1**-**4** occurred in situ cycloaddition reactions to form three different ligands **L$^{1-3}$**.

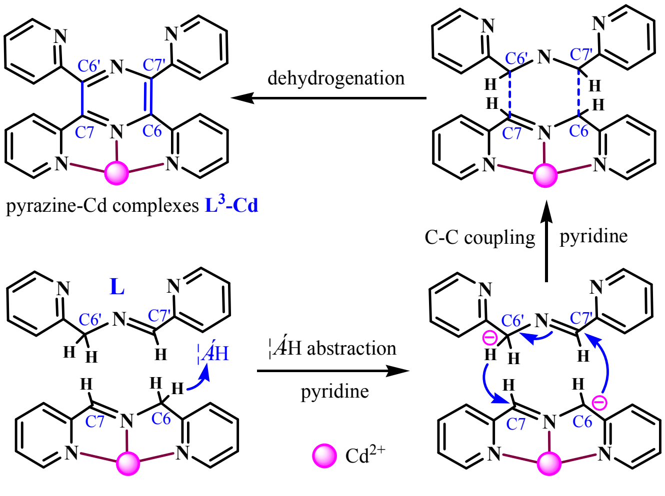
On the basis of the literatures,[8] two possible mechanisms should be addressed in Schemes **2** and **3**. At the stage of low temperature (60°C), we think that the formation of ligand L^1 resulted from [3+2] cycloaddition of Schiff base N-(2-pyridylmethyl)-pyridine-2-carbaldimine (**L**) mediated by Cd^{2+}. It is known that the acidity of a C-H bond in the *α*-position to an imino group -CH=N-CH- is markedly increased if the imino nitrogen atom is coordinated to a metal center.[8] Basic acceptors, such as pyridines, have the ability to deprotonate the imino carbon-bound hydrogen atom to form 1,3-dipole. According to the calssification of Huisgen, the 1,3-dipole of C=N$^+$-C$^-$ can be represented as X=Y$^+$-Z$^-$ of allylic type. To the best of our knowledge, the 1,3-dipolar cycloaddition is also a general and powerful method for the synthesis of five-membered heterocyclic compounds.[9] Such the carbanion formed at C6′ attached C7 atom from another ligand L to form one C-C bond. Meanwhile, due to steric hindrance from the coordination of N1′ to Cd^{II} center, N2 with negative charge attacked C7′ atom from another ligand L to form one C-N bond, finishing [3+2] cycloaddition reaction to give ligand L^1 with half-*chair* configuration imidazolidine-core (Scheme **2**).[10] However, accompanied by a temperature rise and the addition of oxidant H$_2$O$_2$, the center imidazoldine ring was oxidized and dehydrogenated into planar imidazole-core ring with *tetra*-2-pyridyl



Scheme **2** Proposed mechanism for the formation of *tetra*-substituted 2-pyridyl imidazolidine L^1/imidazolium (L^2)$^-$ in the cadmium(II) complexes **1-2**. Reaction conditions: ① α-H abstraction/pyridine, 60°C. ② [3+2] cycloaddition/H$^+$, 60°C. ③ rearrangement and dehydrogenated in presence of with H_2O_2, 100°C.

substituents,[11] accompanied by the carbonylation of the methylene linked in 3-position and protonation of the pyridine nitrogen atom, further forming ligand (L^2)$^-$ (Scheme **2**).

At the stage of high temperature (80°C above), at first the Schiff base **L** coordinated to the cadmium center, followed by the deprotonation of the methylene proton (α-H) by the base (pyridine) to produce a strong nucleophilic carbanion formed at C6. Subsequently, carbanion nucleophilic attacks the electrophilic carbon C7′ from an uncoordinated/coordinated ligand L to form C-C bond, which increases the acidity of a C-H bond at the heterocyclic carbon C6′ atom (*α*-position), and easily produces new carbanion formed at C6′ to finish next nucleophilic attack at the imino carbon C7, simultaneously resulting in another C-C bond coupling and complishing [3+3] cycloaddition reaction.[1,2,12] Finally, the dehydrogenation reaction in the presence of a base pyridine provides compound **4** with an imidazolidine-core *tetra*-substituents L^3, or compound **3** with the bridging effect of the coordinated chlorine atoms (Scheme **3**).



Scheme **3** Proposed mechanism for the formation of *tetra*-substituted 2-pyridyl pyrazine **L^3** in the cadmium(II) complexes **3** and **4**.

In order to further support the above proposed reaction mechanism, one control experiment was carried out at the range from 50 to 120°C, in which one similar ligand with the substituted methyl at C7 atom (L′ in Scheme **S1**) was synthesized and the same reaction mediated by Cd^{II} was attempted (see supporting information). The single-crystal analytical result indicates that the reaction of L′ with $CdCl_2$ in methanol containing pyridine always gives only single C-C coupling[7] product **1′** (Figures **S6-7** and Table **S1**), and fully showing rationality of the proposed C-C coupling reaction mechanism in Schemes **2**-**3**.

Structure and formation mechanism of complex 5

Interestingly, in the presence of one equivalent 2-pyridylethyl-amine, reaction of ligand L with $CdCl_2$ generated pale-yellow dinuclear compound **5** for three days. X-ray single-crystal diffraction confirms its component of $[Cd_2(\mathbf{L^4})Cl_2]\cdot CH_3OH\cdot 0.5H_2O$ (**5**) with in situ formed ligand L^4 bearing imidazole-core, and its molecular structure is shown in Figure **5**. Crystal structural analysis shows that molecule of **5** contains two crystallographically independent penta-coordinated cadmium(II) atoms with the distorted trigonal bipyramidal geometries for Cd1 and Cd2 atoms (see Table **S2** for bond lengths and angles), two in situ formed ligands L^4, two terminal coordinated chlorine atoms, one uncoordinated methanol molecule and half a lattice water molecule. Each ligand L^4 having imidazole-core ring is different from the ligand L^1 with imidazolidine-core ring in **1**, presenting tetra-dentate μ_2-η^1:η^1:η^1:η^1 coordination mode. In addition, π···π packing interaction between two parallel pyridyl rings with two centroid separation of 3.536 Å from two ligands L^4 further stabilizes the dinuclear molecule. And intermolecular hydrogen bonding C-H···Cl interactions result in the assembly of 3-D supramolecular network (Table **S3** and Figure **S8**).

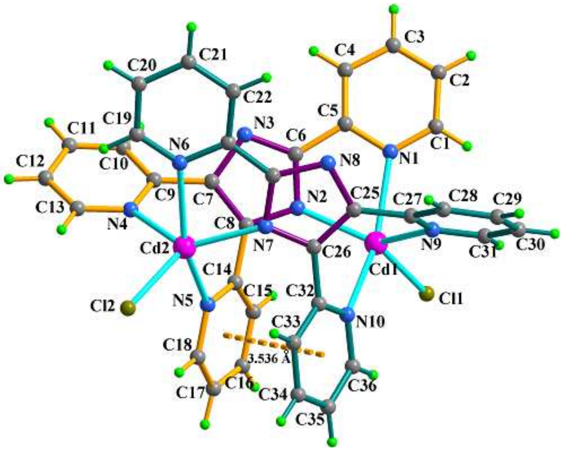
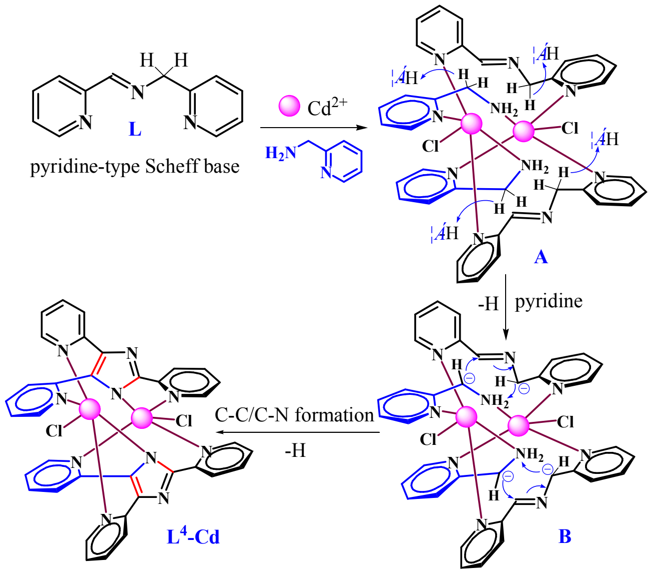


Figure **5**. Molecular structure of the cadmium(II) complex **5** with atomic labels, and the uncoordinated methanol and lattice water molecules are omitted for clarity. Yellow dash line represents intramolecular π···π packing interaction between two almost parallel pyridine rings.

Although the synthesis and structure of ligand HL^4 were once reported by two literatures,[13] no example involves the solvothermal in situ metal-ligand reaction and its coordination chemistry. Accordingly, the in situ formation mechanism of HL^4 is proposed in Scheme **4**. At first Schiff base ligand L and 2-pyridyl-ethylamine



Scheme **4** Proposed mechanism for the formation of 2,2',2"-(1H-imidazole-2,4,5-triyl)-tripyrid-ine (**HL^4**) in the cadmium(II) complex **6**.

co-coordinated to cadmium(II) ions to generate the intermediate **A**, and then due to coordination effect, α-H atoms of Schiff base ligand **L** and 2-pyridylethylamine are activated to readily generate carbanion **B** intermediate in the presence of the base (pyridine), which further facilitates intra-molecular nucleophilic attacks at the imino carbons from Schiff base **L** and the amino nitrogen from 2-pyridylethylamine to form C-C and C-N bonds, finally completing [3+2] cycloaddition reaction and offering compound **5** containing *tri*-substituted 2-pyridyl imidazole HL^4 after dehydrogenation. Similarly, both ligands L^3 and HL^4 can be also successfully isolated from the reactions of those compounds containing corresponding ligands with Na$_2$S.[14]

Structure and formation mechanism of Complexes 6-8

Changing the reactants again, in existence of one equivalent 2-pyridine formaldehyde, ligand **L** reacted with equivalent CdCl$_2$ to offer three 0-D compounds **6-8** containing ligands **L$^{5-6}$** at the range from 80-135°C and one 2-D layer-like compound [Cd$_2$L^{3}Cl$_3$(pic)]$_n$ (**9**) containing ligand L^3 accompanied by H$_2$O$_2$ oxidation of pyridine formaldehyde into picolinate (pic) at more than 80°C, respectively. **6** crystallized as pale yellow crystals suitable for X-ray structure analysis (Figure **6**). The mononuclear complex **6** has an essentially undistorted square pyramidal coordination geometry around the cadmium(II) ion satisfied by three nitrogen atoms (N1, N2, N4) from in situ formed ligand L^5 and two terminal coordinated chlorine atoms (Cl1, Cl2). The Cd-N bond of 2.240(5)-2.477(5) Å), and Cd-Cl (2.416(2)-2.468(2) Å) bond distances are in the range expected for this coordination geometry with cadmium (II). Due to intermolecular hydrogen bonding C-H⋯Cl and π⋯π packing interactions, 2-D layer-like structure is assembled (Figure **S9** and Table **S3**).

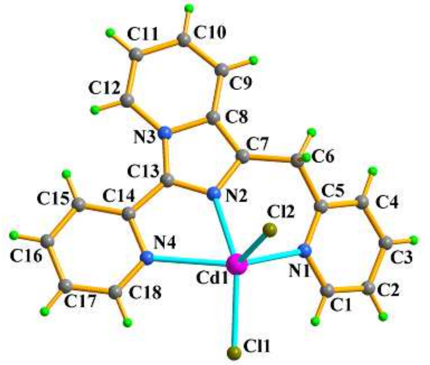


Figure **6**. Molecular structure of the cadmium(II) complex **6** with atomic labels.

Single-crystal X-ray diffraction reveals that compound **7** crystallizes in the monoclinic crystal system of the space group *C*2/*c*.

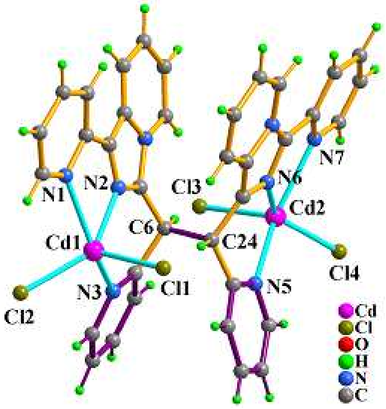


Figure **7** Molecular structure of the cadmium(II) complex **7** containing *cis*-L^6 with partial atom labels. The uncoordinated methanol is omitted for clarity.

As shown in Figure **7**, the molecule of **7** contains two crystallographically independent Cd(II) ions, one in situ formed ligand L^6, two terminal Cl$^-$ ions and one lattice methanol molecule. Each Cd(II) ion is penta-coordinated by three nitrogen atoms (N1, N2, N3/N5, N6, N7) from the same ligand L^6 and two terminal chloride atoms (Cl1, Cl2/Cl3, Cl4). One ligand L^6, which adopts *cis*-conformation of four coordinated terminal groups referred to C6-C24 single bond, coordinates to 2 equiv of Cd^{2+} ions, showing μ_2-η^1:η^1:η^1:η^1:η^1:η^1 coordination mode. Meanwhile, the existence of intermolecular hydrogen bonding C(O)-H⋯Cl interactions makes dinuclear molecular unit [Cd$_2$(*cis*-**L^6**)Cl$_4$] to be assembled into 3-D supramolecular network as shown in Figure **S10**.

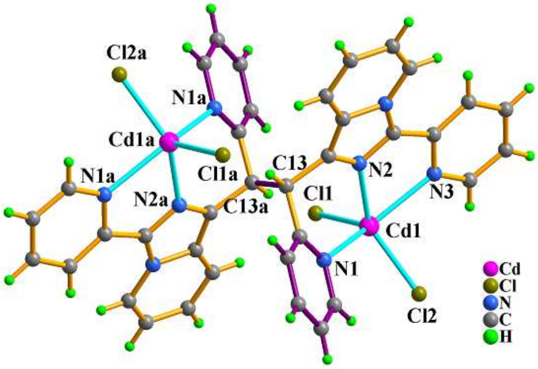
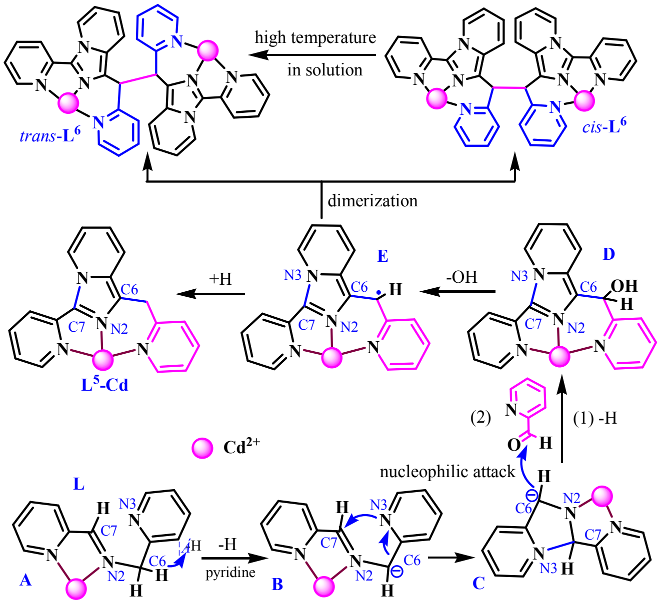


Figure **8** Molecular structure of the cadmium(II) complex **8** with partial atom labels. The symmetric code: a) -x,2-y,2-z.

However, compound **8** crystallizes in the triclinic crystal system of the space group *P*-1. As shown in Figure **8**, the molecule of **8** possesses a crystallographically imposed inversion center located at the mid-point of C13-C13a single bond. Cd1 ion is penta-coordinated by three nitrogen atoms (N1, N2, N3) from the same ligand L^6 and two terminal chloride atoms (Cl1, Cl2) and structurally similar to that of dinuclear **7**. One ligand L^6, which is *trans*-conformation of four coordinated terminal groups referred to C13-C13a bond, coordinates to 2 equiv of Cd^{2+} ions showing $\mu_2\text{-}\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$ coordination mode. Meanwhile, the existence of intermolecular hydrogen bonding C-H···Cl and π···π packing interactions makes dinuclear molecular $[Cd_2L^6Cl_4]$ unit to be assembled into 2-D supramolecular layer with the thickness of 0.681Å as shown in Figure **S11**.



Scheme **5** Proposed mechanism for the in-situ formation of ligands $L^{5\text{-}6}$ in the cadmium(II) complexes **6-8**.

For ligands $L^{5\text{-}6}$, the possible formation mechanism is outlined in Scheme **5**.[7,15] Initially, the carbanion formed at C6 atom from the intermediate **B** increases the nucleophility at the heterocyclic nitrogen atom N3, which facilitates a nucleophilic attack at the imino carbon C7 to form C-N bond,[16] resulting in the formation of intermediate **C**. And then coordination of the nitrogen atom of picolinaldehyde to Cd^{2+} enhances the electrophilicity of the carbon atom of the aldehyde, triggering the formation of an alcoholic intermediate **D** via the nucleophilic attack of **C** to the carbonyl electrophile. Finally, cleavage of the C−O bond in **D** gives a radical intermediate **E**, next two competitive reactions may occur for **E**, which subsequently either obtaining proton from intermediate **A** to furnish the formation of ligand L^5, or undergoing dimerization to give L^6. Because of the free rotation of C-C (C6-C24 for **7** and C13-C13a for **8**) single bond and the steric hindrance from its four connecting groups, ligand L^6 shows two conformations of *cis-*/*trans*-form in formed compounds referring to C-C single bond such as complex **7** (*cis*-form, dynamic stability) and **8** (*trans*-form, thermodynamic stability). Moreover, by increasing reaction temperature or prolonging reaction time, complex **7** may be irreversibly transformed into **8**.

Similar to the above control experiment, reaction of ligand L′ with $CdCl_2$ and KSCN in the presence of one equivalent 2-pyridine formaldehyde always provides single 1-D product **2′** for 50-120°C (Figure **S12** and Table **S1**), also further displaying that the proposed C-N formation mechanism in Scheme **5** is reasonable.

Synthesis and Structure of Complex 9

X-ray single-crystal diffraction reveals that compound **9** exhibits a 2-D layer-like structure with 4^4 topology (Figure **9**(**iii**)-(**iv**)). The asymmetric unit of **9** involves two Cd^{2+} ions, one in situ formed L^3 ligand, and three Cl^- ions (Figure **9**(**i**)). The central Cd1 atom was hepta-coordinated by three bridging chlorine atoms (Cl1, Cl2 Cl2a), three nitrogen atoms from one L^3 ligand (N1, N2, N3), and one oxygen atom from picolinate, displaying distorted decahedral

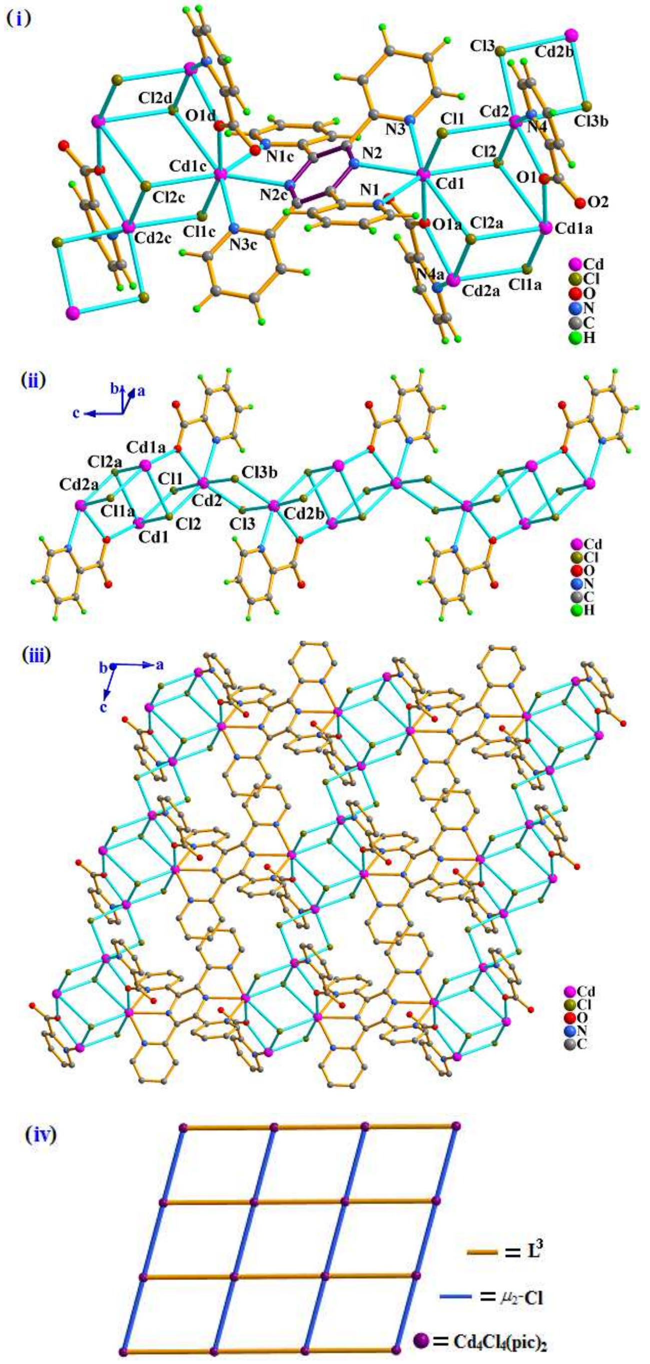


Figure **9**. In **9**, (i) different coordination environment of two Cd^{2+} ions and coordination mode $\mu_2\text{-}\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$ of sexa-dentate ligand L^3, (ii) 1-D $[Cd_4Cl_6\text{-}(pic)_2]_n$ along *c* axis, (iii)-(iv) 2-D layer with 4^4 topology. Symmetric codes: (a) 2-x,-y,1-z; (b) 2-x,-y,-z; (c) 1-x,-y,1-z; (d) -1+x,y,z.

geometry (Figure **S11a** in SI). However, the Cd2 atom sexa-coordinated via four μ_2-bridging chlorine atoms (Cl1, Cl2 Cl3, Cl3b), one nitrogen and oxygen atoms from the same picninate (N4, O1), showing slightly distorted octahedral coordination geometry (Figure **S11b** in SI). Through the bridges of two μ_2-O1, two μ_2-Cl1 and two μ_3-Cl2 atoms, four Cd^{II} atoms(Cd1, Cd1a, Cd2, Cd2a) were linked to form the tetra-nuclear Cd-cluster unit $[Cd_4(\mu_2\text{-}O)_2(\mu_2\text{-}Cl)_2(\mu_3\text{-}Cl)_2]$ with the distances between two adjacent Cd atoms from 3.862 to 3.888 Å (Figure **S11c**), which further assembled into a 1-D infinite cluster chain structure $[Cd_4(\mu_2\text{-}O)_2(\mu_2\text{-}Cl)_2(\mu_3\text{-}Cl)_2]_n$ running along the *c*-axis via double bridging μ_2-Cl3 atoms (Figure **9**(**ii**)). The in situ formed ligand L^3 in **9** has the same coordination mode **II** similar to that in **2**, μ_2-η^1:η^1:η^1:η^1:η^1:η^1, namely, which as a bridging ligand uses its four pyridyl nitrogen (N1, N3, N1c, N3c) and two pyrzinyl nitrogen atoms (N2, N2c) to bridge two Cd^{II} atoms from two adjacent 1-D Cd^{II}-cluster chains, further resulting in the formation of a 2-D layer with 4^4 topology as depicted in Figure **9**(**iii**)-(**iv**).

In the assembly process of complex **9**, due to high reaction temperature (more than 80°C), the added pyridine formaldehyde did not involved in the solvothermal in situ Cd^{II}-L conversion reaction into L^3, and was in situ oxidized to picolinate, participating in the assembly of **9**.

Photophysical properties

The preliminary photoluminescent properties of complexes **1**-**9** and ligands L$^{1\text{-}6}$ in the solid state at room temperature have been investigated and are shown in Figure **S13**. The emission spectra of the complexes 1-9 respectively resemble that of the ligands L$^{1\text{-}6}$ excluding the emission intensity, indicating the fluorescence of the complexes **1**-**9** are L-based emission. Clearly, **1** exhibits green emission with peak wavelengths at 443 nm, while compound **2** and compound **5** present blue emission with peak wavelength at 448 nm and 412 nm, respectively. Similar to the center of the five-membered ring, the different performance among the **1**, **2** and **5**, which could be caused by better rigidity for **2** and **5**. The emission spectra of **3**, **4** and **9** with the same ligand **3** excited at about 390 nm exhibit the different luminescence characteristics: **3** and **4** has the similar emission peak at 436 and 431 nm, but complex **9** has strong emission peak at 451 nm that can tentatively be rationalized by the robust 2-D valence-bonded framework (in **9**). Interestingly, the emission wavelength of complexes **6**-**8** decreased gradually. Accordingly, the spectral differences among the three complexes are intrinsic, and could plausibly be due to the aforementioned structural variation.

Conclusions

In summary, the convenient C-C/C-N bond-forming methodology toward six N-rich heterocycles from Cd^{II}-mediated in situ conversion of pyridine-type Schiff base and the coordination chemistry of nine corresponding Cd^{II}-complexes were systematically explored at the first time. The results show that the in-situ formation of L$^{1\text{-}6}$ not only involved Cd^{II}-catalyzed [3+3]/[3+2] cycloaddition reactions, but also was closely related to the reaction temperature. Meanwhile, to the best of our knowledge, in-situ forming heterocyclic rings L$^{1\text{-}2}$ as well as *cis*-L^6 are also firstly reported. Obviously, the coordination-induced effect presented here offers the intriguing possibility of preparing a series of new asymmetric nitrogen heterocyclic rings displaced from the metals. Moreover, extension of these functional two-, three-, four-connected in situ formed aza-heterocyclic ligands to other metal salts and a further systematic investigation of their function are in progress.

Experimental section

Materials and characterizations

All materials were reagent grade obtained from commercial sources and used without further purification, solvents were dried by standard procedures. Elemental analyses for C, H, N were performed on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded on a Nicolet FT-IR-170SX spectrophotometer in KBr pellets. Thermogravimetric analyses were performed on Perkin-Elmer TGA7 analyzer with a heating rate of 10 °C/min in flowing air atmosphere. The luminescent spectra for the solid state were recorded at room temperature on Hitachi F-2500 and Edinburgh-FLS-920 with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5.0 nm. UV−vis absorption spectra were recorded on a Shimadzu UV1800 UV−vis spectrophotometer. X-ray powder diffraction patterns were measured on a Bruker D8 Advance diffractometer at 40 kV and 40 mA with a Cu target tube and a graphite monochromator. Nitrogen and hydrogen adsorption isotherms were taken on a Beckman Coulter SA 3100 surface area and pore size analyzer.

X-ray Data Collection and Structure Refinement

Complexes **1**-**9** were characterized by single crystal X-ray diffraction. Suitable single crystals were mounted on a glass fiber and the intensity data were collected on a Bruker APEX II diffractometer at 298 K using graphite monochromatic Mo-Ka radiation (λ = 0.71073 Å). Absorption corrections were applied using the multi-scan program SADABS.[17] Structural solutions and full-matrix least-squares refinements based on F^2 were performed with the SHELXS-97[18] and SHELXL-97[19] program packages, respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms on organic ligands were generated by the riding mode (C-H 0.96 Å). A summary of the parameters for the data collection and refinements for nine complexes are given in Table **S1**. Selected bond lengths and angles for complexes **1**-**9** are listed in Table **S2**. CCDC reference numbers for **1**-**9** are CCDC 1022100, 1022101, 987353, 987352, 987351, 987347, 1022102, 1022103 and 987349, respectively. And the others are 1022104 and 1022105 for **1′** and **2′**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Syntheses of complexes 1-9

Synthesis of **1**: A mixture of N-(2-pyridylmethyl)pyridine-2-carbaldimine(L) (0.0394 g, 0.2 mmol), $CdCl_2$ (0.0402 g, 0.2 mmol), MeOH (7 mL) and pyridine (3 mL) was sealed in a 15 mL Pyrex tube. The tube was heated for 3 days at 60 °C under autogenous pressure, and then slow cooling of the resultant solution to room temperature over 24 h gave pale yellow block single crystals of **1**. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 76% (based on Cd). Elemental analysis calcd (%) for $C_{72}H_{70}Cd_7Cl_{14}N_{18}O_2$: C, 34.52; H, 2.80; N, 10.07. Found: C, 34.47; H, 2.89; N, 10.05. IR frequencies (KBr, cm^{-1}): 3447(s), 2957(w), 2367(w), 1638(s), 1566(s), 1420(s), 1329(s), 1260(w), 1155 (s), 1053(w), 1016 (w), 924(w), 880(w), 779(s), 714(w), 650 (w), 517(s), 463(w).

Synthesis of **2**: A mixture of N-(2-pyridylmethyl)pyridine-2-carbaldimine(L) (0.0788 g, 0.4 mmol), $CdCl_2$ (0.0402 g, 0.2 mmol), H_2O_2 (0.1mL, 30%)， MeOH (7 mL) and pyridine (3 mL) was sealed in a 15 mL Pyrex tube. The tube was heated for 3 days at 100 °C under autogenous pressure, and then slow cooling of the resultant solution to room temperature over 24 h gave pale yellow block single crystals of **2**. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 58% (based on Cd). Elemental analysis calcd (%) for $C_{50}H_{42}Cd_2Cl_2N_{12}O_4$: C, 51.25; H, 3.59; N, 14.35. Found: C, 51.18; H, 3.64; N, 14.36. IR frequencies (KBr, cm^{-1}): 3447(s,br), 2957(w), 2363(m), 2041(w), 1773(w), 1638(s), 1560 (s), 1477 (m), 1419 (s), 1327 (s), 1157 (m), 916 (m), 877 (w), 779 (s), 704 (w), 669 (w), 517(s), 463(w).

Synthesis of **3**: the preparation procedure is similar to that of compound **2** except that the temperature is 80°C without oxidant. Finally, **3** is pale yellow crystals with yield 33% (based on Cd). Elemental analysis calcd (%) for $C_{48}H_{32}Cd_2Cl_4N_{12}$: C, 50.37; H, 2.80; N, 14.69. Found: C, 50.28; H, 2.83; N, 14.65. IR frequencies (KBr, cm^{-1}): 3431 (s,br), 2957(m), 2371(s), 2060(s), 1638(s), 1570(s), 1420(s), 1339(s), 1258(w), 1194(w), 1153(m), 1007(m), 924(w), 878(w), 779(s), 648(w), 621(m), 563(w), 516(s).

Synthesis of **4**: the preparation procedure is similar to that of compound **3** except the ratio of ligand and $CdCl_2$ being adjusted to 1:1. Finally **4** is pale yellow crystals with yield 45% (based on Cd). Elemental analysis calcd (%) for $C_{24}H_{18}Cd_2Cl_4N_6O$: C, 39.25; H, 2.45; N, 11.45. Found: C, 39.28; H, 2.43; N, 11.55. IR frequencies (KBr, cm^{-1}): 3431(s), 2957(m), 2332(w), 2112(s), 1854(w), 1653(s), 1638(s), 1568(s), 1429(s), 1404(s), 1339(m), 1254(w), 1196(w), 1150(m), 1011(m), 924(w), 878(w), 779(s), 750(w), 718(w), 635(m), 559(m), 517(m), 465(w).

Synthesis of **5**: the preparation procedure is similar to that of compound **4** except more addition with 2-pyridylethyl-amine (0. 0216g, 0.2 mmol). Finally, **5** is pale yellow crystals with yield 35% (based on Cd). Elemental analysis calcd (%) for $C_{74}H_{58}Cd_4Cl_4N_{20}O_3$: C, 47.49; H, 3.10; N, 14.97. Found: C, 47.38; H, 3.03; N, 15.05. IR frequencies (KBr, cm^{-1}): 3447(s,br), 2957(w), 2367(w), 2041(w), 1647(s), 1560(s), 1522(w), 1483(w), 1431(s), 1327(s), 1258(w), 1152(m), 1013(m), 976(w), 878(w), 843(w), 779(s), 719(m), 650(w), 517(m), 459(w).

Synthesis of **6**: the preparation procedure is similar to that of compound **4** except more addition with picolinaldehyde (0. 0214g, 0.2 mmol) and at N_2 atmosphere. Finally, **6** is pale yellow crystals with yield 68% (based on Cd). Elemental analysis calcd (%) for $C_{18}H_{14}CdCl_2N_4$: C, 45.99; H, 2.98; N, 11.92. Found: C, 45.93; H, 2.99; N, 11.95. IR frequencies (KBr, cm^{-1}): 3422(s,br), 2957(w), 2372(w), 1638(s), 1593(m), 1560(s), 1487(m), 1418(s), 1375(w), 1339(m), 1254(w), 1169(m), 1074(w), 999(w), 843(w), 781(s), 760(w), 681(w), 633(m), 517(m), 463(w).

Synthesis of **7**: the preparation procedure is similar to that of compound **6** except the temperature up to 100 **°C**. Finally, **7** is pale yellow crystals with yield 53% (based on Cd). Elemental analysis calcd (%) for $C_{37}H_{31}Cd_2Cl_4N_8O$: C, 45.76; H, 3.19; N, 11.54. Found: C, 45.69; H, 3.28; N, 11.56. IR frequencies (KBr, cm^{-1}): 3431(s), 2957(w), 2363(m), 2064(m), 1639(s), 1595(s), 1560(s), 1489(m), 1420(m), 1325(m), 1256(w), 1155(m), 1007(w), 878(w), 777(m), 623(w), 517(s).

Synthesis of **8**: the preparation procedure is similar to that of compound **6** except the temperature 120 **°C**. Finally, **8** is pale yellow crystals with yield 58% (based on Cd). Elemental analysis calcd (%) for $C_{36}H_{26}Cd_2Cl_4N_8$: C, 46.09; H, 2.77; N, 11.95. Found: C, 46.05; H, 2.73; N, 11.91. IR frequencies (KBr, cm^{-1}): 3447(s,br), 2957(w), 2363(w), 1639(s), 1595(s), 1560(s), 1522(w), 1487(m), 1420(m), 1339(m), 1258(w), 1190(w), 1153(w), 1080(m), 1003(m), 878(w), 799(s), 743(w), 692(m), 652(w), 517(m).

Synthesis of **9**: the preparation procedure is similar to that of compound **4** except more addition of H_2O_2. Finally, **9** is pale yellow crystals with yield 72% (based on Cd). Elemental analysis calcd (%) for $C_{18}H_{12}Cd_2Cl_3N_4O_2$: C, 33.36; H, 1.85; N, 8.65. Found: C, 33.28; H, 1.88; N, 8.58. IR frequencies (KBr, cm^{-1}): 3414(s,br), 2926(w), 2851(w), 2369(w), 2137(w), 2066(m), 1639(s), 1560(s), 1420(s), 1325(m), 1260(w), 1151(m), 1018(w), 777(m), 712(w), 638(w), 519(s).

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