Formation and conversion of six temperature-dependent fluorescent Zn\textsuperscript{II}-complexes containing two \textit{in situ} formed N-rich heterocyclic ligands\textsuperscript{†}

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Six temperature-dependent Zn(II) complexes 1–6 based on the simple Schiff base 1\textsuperscript{a} from condensation of equivalent 2-pyridine formaldehyde (2-Pfd) and 2-pyridylethylamine (2-Pea) were systematically studied for the first time. These six complexes are: two complexes of Zn\textsubscript{2}L\textsubscript{1} (1 and 2) involving in \textit{in situ} formed N-rich heterocyclic ligand L\textsubscript{1} at 80 °C; two complexes of [Zn\textsubscript{2}(cis-L\textsubscript{1})\textsubscript{X\textsubscript{3}}] (S = H\textsubscript{2}O for 3, S = O for 5) involving in \textit{in situ} formed azaheterocyclic ligand cis-L\textsubscript{1} at 100 °C, and the rest two ones of [[Zn\textsubscript{2}(trans-L\textsubscript{1})\textsubscript{X\textsubscript{4}}] (4 and 6) involving in \textit{in situ} formed azaheterocyclic ligand trans-L\textsubscript{1} at 120 °C (where X = Cl (1, 3, 4) and N\textsubscript{2} (2, 5, 6)). L\textsubscript{1} = N-(2-pyridylmethoxy)-pyridine-2-carbaldimine, L\textsubscript{2} = 1-pyridineimidazo-[1,5-a]pyridine, L\textsubscript{3} = 1-(1,2-di(pyridin-2-yl)-2-(3-(pyridin-2-yl)imidazo-[1,5-a]-pyridin-1-yl-ethyl)-3-(pyridin-2-yl)imidazo-[1,5-a]pyridine). Interestingly, three Cl-based complexes 1, 3, 4 under appropriate conditions can be irreversibly translated into the corresponding N\textsubscript{2}-based 2, 5, 6, respectively. The possible formation/conversion mechanism shows that the α-H activation in -CH\textsubscript{2}–N–CH\textsubscript{2}– moiety of L\textsubscript{1} coordinated to Zn\textsuperscript{2+} ion should be the original driving force for the intermolecular C–C/C–N coupling and ring formation reactions, meanwhile reaction temperature also plays a very important role during the formation/conversion of 1–6. Moreover, the results indicate that complexes 1–6 have good fluorescence properties as potential fluorescent materials.

Introduction

The C–H bond in the α-position to an imino group –CH\textsubscript{2}–N–CH\textsubscript{2}– is activated after the imino nitrogen atom is coordinated to a metal center.\textsuperscript{1} Basic acceptors, such as pyridine, imidazole, etc., have the ability to deprotonate the imino carbon-bound hydrogen atom to form 1,3-dipole. According to the classification of Huisgen, the 1,3-dipole of C=C=N–C\textsuperscript{−} can be represented as X=Y=Z of allylic type.\textsuperscript{2} Schiff base N-(2-pyridylmethyl)-pyridine-2-carbaldimine (L\textsubscript{1}) with bipyridyl groups, condensed from equivalent 2-pyridine formaldehyde (2-Pfd) and 2-pyridylethylamine (2-Pea), may be led to various N-rich heterocyclic products under the guidance of the metal ion coordination induced effect, e.g. titanium(III), iron(II) and nickel(II) complexes containing 2,3,5,6-tetra-(pyridin-2-yl)piperazine/pyrrole\textsuperscript{3} as well as cadmium(II) complexes with 2,2′,6′,2″-tetra-(1-(pyridin-2-ylmethyl)imidazolidine-2,4,5-triypryidin\textsuperscript{4} are typical examples of such products.

Obviously, \textit{in situ} formation of these N-rich heterocycles and their derivatives is very important in various fields: (i) azaheterocycles in organic syntheses can act as protective groups, since they are particularly easy to hydrolyze in acidic solutions and are stable in basic solutions. (ii) Some azaheterocycles can be used as intermediates in the biosynthesis of nucleotides, avoiding the shortcomings of traditional synthesis methods, and some of their metal complexes are found to be active as cytotoxic metallopharmaceuticals.\textsuperscript{5} (iii) They are important building blocks in biologically active compounds and carriers of pharmacologically active carbonyl compounds, and some of metal complexes are potential chemotherapeutic agents for DNA cleavage.\textsuperscript{6} (iv) Their transition-metal complexes have been also extensively studied for applications in OLEDs, luminescent materials,\textsuperscript{7} etc. Hence, it is very meaningful to explore the formation conditions and coordination behaviors of multi-substituted N-rich heterocycles by solvothermal \textit{in situ} metal-induced reaction from simple Schiff base ligands. Herein we report the syntheses and their subsequent coordination
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Experimental section

Materials and methods

All reagent were grade obtained from commercial sources and used without further purification. Solvents were dried by the standard procedures. Elemental analyses for C, H, N were performed on a Perkin-Elmer TGA7 analyzer with a heating rate of 10 °C min⁻¹ in flowing air atmosphere. The solid state luminescent spectra 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. X-ray powder diffraction patterns were measured on a Bruker D8 Advance diffractometer at 40 kV and 40 mA with a Cu target and a graphite monochromator. Nitrogen and hydrogen adsorption isotherms were taken on a Belsorp-Max surface area and pore size analyzer.

Synthesis of L¹

For complexes 1–6, they were prepared by a similar procedure except reaction temperature and auxiliary ligand Na₃N₄. A mixture of N-(2-pyridylmethyl)pyridine-2-carbaldimine (L¹) (0.0394 g, 0.2 mmol), ZnCl₂ (0.0402 g, 0.2 mmol), 2-pyridine formaldehyde (0.022 g, 0.2 mmol), DMF (7 mL) and pyridine (3 mL) was sealed in a 15 mL Pyrex tube. The tube was heated for 3 days under autogenous pressure, and then slowly cooled the reaction solution to room temperature over 24 h and filtered to give pale yellow block single crystals for 1 at 80 °C, 3 at 100 °C and 4 at 120 °C. When Na₃N₄ (0.130 g, 0.4 mmol) was added to the collected filtrate, three new complexes 2 (80 °C), 5 (100 °C) and 6 (120 °C) were obtained under the same reaction conditions, respectively. The crystals were collected by filtration, washed with Et₂O (2 × 3 mL), and dried in air (Table 1).

Syntheses of complexes 1–6

ZnL²Cl₂ (1). Yield: 75% (based on Zn). Elemental analysis calcd (%) for C₁₈H₁₄ZnCl₂N₄: C, 51.11; H, 3.31; N, 13.25. Found: C, 51.07; H, 3.36; N, 13.27. IR frequencies (KBr, cm⁻¹): 3562–3443(br, s), 2959(w), 2370(w), 1635(m), 1596(s), 1561(s), 1486(m), 1419(s), 1376(w), 1340(m), 1252(w), 1171(m), 1073(w), 1002(w), 847(w), 782(m), 763(w), 682(m), 635(w), 519(w), 467(w).

ZnL²(N₃)₂ (2). Yield: 69% (based on Zn). Elemental analysis calcd (%) for C₁₈H₁₄ZnCl₂N₄: C, 49.59; H, 3.21; N, 32.13. Found: C, 49.59; H, 3.24; N, 32.09. IR frequencies (KBr, cm⁻¹): 3563–3448(br, s), 2959(w), 2798(s), 2063(m), 1636(s), 1597(s), 1540(s), 1470(vs), 1445(s), 1342(vs), 1291(s), 1187(s), 1151(s), 1022(w), 902(vs), 793(s), 765(m), 675(m), 637(m), 601(w), 572(m), 529(m), 463(w).

ZnL³Cl₂·H₂O (3). Yield 75% (based on Zn). Elemental analysis calcd (%) for C₃₆H₂₆ZnCl₂N₈O: C, 50.16; H, 3.25; N, 13.01. Found: C, 50.18; H, 3.27; N, 13.05. IR frequencies (KBr, cm⁻¹): 3561–3443(br, s), 2955(m), 2782(s), 2063(m), 1635(vs), 1597(m), 1540(s), 1470(vs), 1445(s), 1342(vs), 1291(s), 1188(vs), 1151(s), 1022(w), 902(vs), 793(s), 765(m), 675(m), 637(m), 601(w), 572(m), 529(m), 463(w).

ZnL³Cl₂·3H₂O (4). Yield 67% (based on Zn). Elemental analysis calcd (%) for C₃₆H₂₆ZnCl₂N₈O: C, 51.23; H, 3.08; N, 13.28. Found: C, 51.19; H, 3.11; N, 13.33. IR frequencies (KBr, cm⁻¹): 3565–3443(br, s), 2994(m), 2887(m), 2045(m), 1634(s), 1598(vs), 1540(s), 1471(s), 1444(vs), 1347(m), 1290(vs), 1187(s), 1150(vs), 1023(s), 902(s), 794(m), 764(s), 678(m), 635(m), 603(m), 574(w), 525(w), 464(w).

ZnL⁴(N₃)₄ (5). Yield 73% (based on Zn). Elemental analysis calcd (%) for C₃₆H₂₆Zn₂Cl₄N₈: C, 49.68; H, 2.99; N, 32.20. Found: C, 49.65; H, 3.03; N, 32.25. IR frequencies (KBr, cm⁻¹): 3567–3447(br, s), 2956(w), 2366(w), 2062(m), 1649(s), 1561(m), 1523(w), 1482(m), 1433(s), 1341(s), 1259(w), 1151(m), 1012(m), 975(w), 879(w), 844(w), 780(m), 720(m), 651(w), 518(m), 460(w).

ZnL⁵(N₃)₄ (6). Yield 70% (based on Zn). Elemental analysis calcd (%) for C₃₆H₂₆Zn₂Cl₄: C, 49.68; H, 2.99; N, 32.20. Found: C, 49.70; H, 3.03; N, 32.22. IR frequencies (KBr, cm⁻¹): 3566–3446(br, s), 2996(s), 2893(m), 2798(s), 2061(m), 1636(s), 1574(s), 1421(s), 1335(s), 1259(w), 1171(m), 1073(w), 975(w), 879(w), 844(w), 780(w), 763(m), 682(m), 635(w), 519(w), 467(w).
### Results and discussion

#### Syntheses and general characterization of complexes

Pale-yellow crystals of 1–6 (ca. 67–75% yield) were obtained from the *in situ* solvothermal treatment of $N$-(2-pyridylmethyl)-pyridine-2-carbaldimine ($L^1$) with ZnCl$_2$/ZnI$_2$ + NaN$_3$ in the mixed solvents of DMF and pyridine ($v/v = 2:1$) at 80–120 °C for three days (see Scheme 1). The component diversification of the resulting discrete Zn$^{2+}$-$L^1$-$L^3$ complexes 1–6 can be tuned simply by changing reaction temperature, in which *in situ* forming L$^2$/L$^3$ are the results of intermolecular C–C/C–N coupling and ring-forming reactions deriving from $z$-H activation at ortho-position of imine –CH$_2$N=CH$_2$– moiety reduced by Zn(II) coordination (possible *in situ* forming mechanism in Scheme S1†). Elemental analysis and PXRD (Fig. S1 in the ESI†) confirmed the phase purity of the bulk materials. Compounds 1–6 are air-stable and insoluble in water and most organic solvents. Meanwhile, stirring reactions of NaN$_3$ and the Cl-based complexes 1, 3 and 4 for 5 hours at 100 and 120 °C, respectively. Or alternatively the direct reaction of L1 with ZnCl$_2$ + NaN$_3$ like the Cl-based complexes 1, 3 and 4 can also give the corresponding N$_3$-based complexes 5 and 6 in high yield, respectively. Or alternatively the direct reaction of L1 with ZnCl$_2$ + NaN$_3$ like the Cl-based complexes 1, 3 and 4 can also give the corresponding N$_3$-based complexes 5 and 6 in high yield, respectively. Alternatively two N$_3$-based complexes 5, 6 can be also obtained via stirring reactions from NaN$_3$ and the corresponding Cl-based complexes 1, 3 and 4 for 5 hours at 100 and 120 °C, respectively.

#### X-ray crystallographic studies

Complexes 1–6 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-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using the multi-scan program SADABS. Structural solutions and full-matrix least-squares refinements based on $F^2$ were performed with the SHELXS-97 (ref. 9) and SHELXL-97 (ref. 10) 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 0.9 Å). For 1 and 3, the SQUEEZE option in PLATON was used to remove the disordered solvent water molecules, and the actual water molecules in the unit cell are determined by elemental and thermo-gravimetric analyses (EA and TGA). 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 1–6 are listed in Table S2.† Hydrogen bond lengths and angles for complex 3 are given in Table S3.† CCDC reference numbers for 1–6 are CCDC 1032239, 1508822, 1032241, 1508812, 1032243 and 1032244, respectively.
transition metal complexes, and the appearance of the $\nu_c$-N$_3$ band at 1341–1342 cm$^{-1}$ indicates the asymmetric nature of the azide groups in three complexes 2, 5, 6.

Thermal stability of six complexes was investigated by the TGA technique (see Fig. S2†). The TG curve for 3 shows two steps of weight loss. The weight loss of the uncoordinated water molecules is observed from 83 to 112 °C for 3 (calc. 2.09% and exp. 1.96%). On further heating, the complexes start to be decomposed at 312 °C for 3. For the remaining five complexes 1, 2, 4, 5 and 6, their TGA curves are also similar and present one step of weight loss, namely decomposition of the complexes are observed at 205 °C for 1, 321 °C for 2, 307 °C for 4, 341 °C for 5 and 343 °C for 6, respectively. Although all six complexes are zero dimensional, their thermal stability is obviously different, probably due to the different dimensions of their supramolecular structures, in which the complex 3 has low dimensional (2D) supramolecular structure and shows the lowest thermal stability (see below for details).

Structural analysis and discussion

$\text{ZnL}_2\text{Cl}_2$ (1). When the reaction of ligand L$^1$ with an equimolar amount of 2-pyridine formaldehyde and ZnCl$_2$ at 80 °C lasted for three days, 0-D compound 1 was obtained. Its asymmetric unit involves one crystallographically independent mononuclear molecule ZnL$_2$Cl$_2$ (Fig. 1), and each molecule has an essentially undistorted square pyramidal coordination geometry around the zinc(n) ion satisfied by three nitrogen atoms (N1, N2, N3) from in situ formed ligand L$^2$ and two terminal coordinated chlorine atoms (Cl1, Cl2). The Zn–N bond length of (2.030(4)–2.385(4) Å), and Zn–Cl (2.2602(14)–2.2626(16) Å) bond distances are in the expected range for this coordination geometry with zinc(n). The ligand L$^2$ shows $\mu_1$–$\eta^1$–$\eta^1$–$\eta^1$ coordination mode. Due to intermolecular hydrogen bonding C–H···Cl and $\pi$···$\pi$ packing interactions (Table S3†), a 2-D supramolecular layer-like structure with 4$^4$ topology is assembled and as indicated in Fig. 2.

$\text{ZnL}_2(\text{N}_3)_2$ (2). When NaN$_3$ is added to the reaction mixture, two coordinated chlorine atoms in 1 are replaced by two azide ions and produce a new complex ZnL$_2$(N$_3$)$_2$ (2) (Fig. 3) at the same reaction temperature. Similar to 1, complex 2 is also a 0-D mononuclear structure, and its asymmetric unit involves one $\text{Zn}\text{L}_2^{2+}$ ion, one in situ formed L$^2$ ligand, and two terminal monodentate $\eta^1$-coordinated N$_3$ ions. The coordination geometry around Zn1 is distorted trigonal bipyrimidal with five nitrogen N atoms (N1, N2, N4, N5, N8) from one L$^2$ ligand and two azide anions, in which N2, N5, N8 atoms are the triangle plane, and N1 and N4 atoms at the apical positions. The ligand L$^2$ in 2 also presents the same coordination mode: $\mu_1$–$\eta^1$–$\eta^1$–$\eta^1$, namely, which as a terminal tridentate ligand using the three nitrogen atoms (N1, N2, N4) on the same side of L$^2$ coordinates to one Zn$^{2+}$ ion to form a 0-D discrete structure. The Zn–N bond distances are 1.950(4)–2.283(3) Å. And intermolecular hydrogen bonding C–H···Cl and $\pi$···$\pi$ stacking interactions (Table S3†) resulting in 3-D supramolecular network with 3$^5$·$4^1$·$5^6$·$6^5$ topology further stabilize crystal structure (Fig. 4).

$\text{Zn}_n(\text{cis-L})^m\text{X}_q$·$\text{S}$. (X = Cl, S = H$_2$O for 3; X = N$_3$, S = 0, for 5). When the temperature of the reaction mixture was gradually elevated to 100 °C, two new complexes 3 and 5 with in situ
formed ring-forming and C–C coupling product L\textsuperscript{3} from ligand L\textsuperscript{2} and 2-pyridine formaldehyde were obtained as the two isologues. Both compounds 3 and 5 are 0-D dinuclear structures with monoclinic P\textsuperscript{2}(1)/c space group.

As shown in Fig. 5, the molecule of 3 with a C\textsubscript{2} rotary axis contains two Zn(n) ions, one in situ formed ligand L\textsuperscript{3}, four terminal Cl\textsuperscript{−} ions and one lattice water molecule. Zn1 atom is penta-coordinated by three nitrogen atoms (N1, N2, N4) from the same ligand L\textsuperscript{3} and two terminal chloride atoms (Cl1, Cl2) and presents a slightly distorted trigonal bipyrimidal coordination geometry. The ligand L\textsuperscript{3}, which adopts cis-conformation of four coordinated terminal groups referred to C\textsubscript{6}–C\textsubscript{6a} single bond and coordinates to two Zn\textsuperscript{2+} ions, shows µ\textsubscript{3}–η\textsuperscript{2}·η\textsuperscript{2}·η\textsuperscript{1}·η\textsuperscript{1}·η\textsuperscript{1} coordination mode. The Zn−N bond length of (2.030(9)–2.323(11) Å), and Zn−Cl (2.220(4)–2.278(5) Å) bond distances are in the range expected for this coordination geometry with zinc(n).

Meanwhile, the existence of intermolecular hydrogen bonding C–H···Cl and π···π packing interactions (Table S3\textsuperscript{†}) makes dinuclear molecular unit Zn\textsubscript{2}(cis-L\textsuperscript{3})Cl\textsubscript{4} to be linked into 1-D wave-like chain, and further assembled into 3-D network via inter-chain hydrogen bond C–H···O as shown in Fig. 6.

Compared with Cl\textsuperscript{−} ion, azide may have different spatial orientation, however compound 5 presents the same P\textsuperscript{2}(1)/c space group. The molecule of 5 consists of two crystallographically independent Zn(II) ions showing a slightly distorted trigonal bipyrimidal coordination geometry, one in situ formed ligand L\textsuperscript{3} with µ\textsubscript{3}·η\textsuperscript{1}·η\textsuperscript{1}·η\textsuperscript{1}·η\textsuperscript{1}·η\textsuperscript{1} coordination mode and four terminal η\textsuperscript{1}·N\textsubscript{3}− ions as depicted in Fig. 7. The Zn−N bond length of 1.955(5)–2.2344(5) Å is consistent with that of complex 3. Because of the hydrogen bonding C–H···N interactions from azide ion and pyridyl rings, each dinuclear molecular unit Zn\textsubscript{2}(cis-L\textsuperscript{3})(N\textsubscript{3})\textsubscript{4} links seven adjacent units to assemble into 3-D supramolecular network. If the dinuclear molecular unit Zn\textsubscript{2}(cis-L\textsuperscript{3})(N\textsubscript{3})\textsubscript{4} viewed as the node and the hydrogen bonding C–H···N interactions (Table S3\textsuperscript{†}) as the linker, the resulting network can be simplified as 3\textsuperscript{3}·4\textsuperscript{10}·5\textsuperscript{6}·6\textsuperscript{2} topology as displayed in Fig. 8.

\[
[[\text{Zn}_2(\text{trans-L}^3)\text{X}_4]]. (X = \text{Cl for 4 and } X = \text{N}_3 \text{ for 6}).
\]

When the reaction temperature finally rising to 120 °C, two complexes 4

![Fig. 4](image-url) In 2, (a) 3-D supramolecular network assembled by intermolecular hydrogen bonding C–H···N and π···π packing interactions in ac plane. (b) 3-D 3\textsuperscript{6}·4\textsuperscript{13}·5\textsuperscript{6}·6\textsuperscript{2} topology.

![Fig. 5](image-url) Molecular structure of compound Zn\textsubscript{2}(cis-L\textsuperscript{3})Cl\textsubscript{4}·H\textsubscript{2}O (3) with atomic labels, and one lattice water molecule was omitted for clarity. The symmetric code: (a) 2 – x, y, 0.5 – z.

![Fig. 6](image-url) In 3, (a) 1-D wave-like chain constructed by inter/intra molecular hydrogen bonding C–H···Cl (blue dashed line) and π···π (plum dashed line) packing interactions along a axis. (b) 3-D supramolecular network assembled by interchain hydrogen bonding C–H···O (blue dashed line) interactions.
and 6 containing in situ formed L\textsuperscript{3} were formed as the two isologues. Both compounds 4 and 6 are 0-D dinuclear structures with monoclinic P\textsuperscript{2}(1)/n space group for 4 and P\textsuperscript{1} space group for 6, respectively.

As shown in Fig. 9, the molecule of 4 possesses a crystallographically imposed inversion center located at the mid-point of C6–C6a single bond (blue color). Zn1 ion is penta-coordinated by three nitrogen atoms (N1, N2, N4) from the ligand L\textsuperscript{3} and two terminal chloride atoms (Cl1, Cl2), demonstrating trigonal bipyrimidal coordination geometry similar to that of its conformational isomer 3. One ligand L\textsuperscript{3}, which is

\( \text{trans}\)-conformation of four coordinated terminal groups referred to C6–C6a bond, coordinates to 2 equiv. of Zn\textsuperscript{2+} ions showing \( \mu_2\cdot\eta^1\cdot\eta^1\cdot\eta^1\cdot\eta^1\) coordination mode. Meanwhile, the existence of intermolecular hydrogen bonding C–H⋅⋅⋅Cl interactions (Table S3\textsuperscript{†}) makes dinuclear molecular [Zn\textsubscript{2}(trans-L\textsuperscript{3})Cl\textsubscript{4}] unit to be assembled into a 3-D supramolecular network with the topology of \( 3\text{\,5}\cdot4\text{\,18}\cdot6\text{\,5} \) as shown in Fig. 10 and 11.

When Cl\textsuperscript{-} ion in complex 4 was completely replaced by azide ion, its isologues 6 was obtained. From Fig. 12, two zinc ions (Zn1 and Zn1a) in 6 have the same coordination pattern of
trigonal bipyramidal coordination geometry as the zinc ions in 4. Meanwhile, replacement of the azide ions have no effect on trans-conformation of the in situ formed L2 ligand in 6. It is to be observed that the varied spatial orientations of azide ions make the supramolecular structure of complex 6 different from that of complex 4, exhibiting a 3-D supramolecular network with the topology of $3^4 \cdot 4^4 \cdot 6^{20}$ through intermolecular hydrogen bonding C–H⋯N and π⋯π packing interactions (Table S3†) as displayed in Fig. 12.

**Structural in situ formation, transformation and temperature effect**

In this contribution, the simple Schiff base ligand L1 with a donor set of N3 was firstly applied in the system of Zn-based aza-heterocyclic complexes. Initial reaction of ZnCl2 at 80 °C with L1 together with 2-pyridine formaldehyde afforded Zn-mono-nuclear compound ZnL2Cl2 \( (1) \) containing one in situ formed N-rich heterocycle L2 with a donor set of N3 via intermolecular C–C/C–N coupling and ring forming reactions (Scheme S1†). And then two terminal coordinated Cl− ions in 1 could be easily replaced by two N3− anions and produced the corresponding mononuclear zinc(II) compound ZnL2[N3]2 (2). Increasing the reaction temperature to 100 °C, Zn2+-induced intermolecular C–C coupling reaction between two L2 molecules resulted in the formation of cis-conformation L3 and the corresponding Cl-based compound [Zn2(cis-L3)Cl2]H2O (3) as well as N3-based substitute [Zn2(cis-L3)[N3]4 (S). Continuing to increase the reaction temperature to 120 °C, in situ formed cis-L3 can be lightly converted to the trans-L3 and the corresponding Cl-based compound Zn2[trans-L3]Cl4 (4) as well as N3-based substitute [Zn2[trans-L3][N3]4 (6) with high thermal stability via the rotation of the C–C single bond derived by reaction temperature.

A careful inspection of experimental condition reveals that the reaction temperature has a significant contribution to final structures of two aza-heterocycles of L2−5 as well as six corresponding Zn-based compounds 1–6, which might mainly depends on the influence of reaction temperature as reaction driving force. When reaction temperature is higher than 80 °C, the ortho-hydrogen atom of an imino group (CH=N–CH) in ligand L1 can be markedly activated by the coordination induction of Zn2+ ion,12 and pyridine as basic acceptor has the ability to deprotonate the imino carbon-bound α-position hydrogen atom and form 1,3-dipolar, leading to the occurrence of inter-molecular C–C/C–N coupling, [3+2] cycloaddition, transformation of cis/trans-isomers caused by C–C single rotation and formation of final Zn-imidazo[1,5-a]pyridine complexes L2/L3–Zn (Scheme S1†).

**Fluorescence/UV absorption spectra and titration of L1** + 2-Pfd

The luminescence properties of complexes 1–6 have been studied in the solid state at room temperature as depicted in Fig. S3.† Observably, 1–6 are blue emission with peak wavelengths at the range from 428 to 450 nm. These emissions could be tentatively assigned as resulting from the ligand-to-metal charge transfer (LMCT).3 Meanwhile, the fluorescence response of receptor L1 towards Zn2+ was studied in 0.10 mM mixture solution of DMF and pyridine (volume ratio of 2 : 1) at the different temperatures. Upon excitation at 355 nm, L1 and 2-pyridine formaldehyde (2-Pfd) (molar ratio of 1 : 1) in DMF and pyridine at 80–120 °C presented dark blue emission at 469 nm which could be attributed to the intra-ligand π⋯π* transition.14 As stepwise addition of ZnCl2 solution in DMF at 80 °C with
concentration ranging from 0.1 equiv. to 2.0 equiv., fluorescent emission of L₁ + 2-Pfd gradually red-shifted to 498 nm with their fluorescent intensity at 498 nm enhanced linearly with the Zn²⁺ concentration and saturated when [Zn²⁺] reached to 1.00 equiv. (Fig. 13). Interaction between Zn²⁺ and L₁ + 2-Pfd was also studied by UV absorption spectra (Fig. S4†). Concomitant addition of ZnCl₂ into L₁ + 2-Pfd in DMF + pyridine causes a new absorption peak at 385 nm with intensity increased while that at 225, 261, 338, 430 nm decreased with four isosbestic points at 247, 272, 305, 348 nm. The binding ratio between Zn²⁺ and ligand was estimated to be 1 : 1 as confirmed by its job plot (Fig. S5†) and the related crystal structures.

As the temperature of the mixture [ZnCl₂ + L₁ + 2-Pfd] increased from 80 °C to 100 °C and 120 °C, the emission peak wavelength of the mixture ZnCl₂ + L₁ + 2-Pfd has an obvious red-shift to 525 nm for 3 (at 100 °C) and 531 nm for 4 (at 120 °C), respectively. The fluorescent intensity for 3 (Fig. S6†) and 4 (Fig. S7†) were both enhanced, but the peak shape were unchanged when compared to that at 80 °C (for 1) due to the formation of 2D/3D dimensional supramolecular network assembled by a large number of intramolecular and intermolecular hydrogen bonding C–H...Cl and/or π-π stacking interactions.

The azide anion substitution effect of Cl-based Zn-complexes 1, 3 and 4 was examined by fluorescence titration of 1/3/4 + NaN₃ at 80 °C, 100 °C and 120 °C, respectively (Fig. 14 and S8 and S9†). The fluorescent intensity of 1/3/4 + NaN₃ was, to some extent, enhanced with almost unchanged peak shape and position compared to the corresponding Cl-based Zn-complexes, in which the further enhanced fluorescent intensity of NaN₃-based Zn-complexes could be attributed to the stronger intermolecular/intramolecular hydrogen bonding interactions supported by more stable and higher dimensional supramolecular structures in the solid state.

In conclusion, this work describes the first example of efficient syntheses and complexation of two asymmetric N-rich heterocyclic ligands (L₂⁻) containing imidazo-[1,5-a]-pyridine core involving solvothermal in situ ligand generation from simple tridentate N₃-set pyridine-type Schiff base ligand (L₁) mediated by Zn²⁺. Further studies on in situ formation and conversion of ligands L₁⁻² and six corresponding Zn-complexes 1–6 show that temperature effect is the key factor rather than anion effect, which can tune their supramolecular connections and topologies of resulting zinc complexes. Obviously, this synthesis strategy may bring a broad interest in the construction of novel nitrogen-rich multidentate asymmetric heterocycles relating to metal ion induced x-H activation chemistry on imine bond –CH=N–, and relevant metal–organic frameworks as well as inorganic–organic hybrid materials with advanced luminescent and biological functions.

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References


8 G. M. Sheldrick, SADABS, Version 2.05, University of Göttingen, Göttingen, Germany.


