Formation and conversion of six temperature-dependent fluorescent ZnII-complexes containing two in situ formed N-rich heterocyclic ligands†

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Six temperature-dependent Zn(II) complexes 1–6 based on the simple Schiff base L1 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 ZnL2X2 (1 and 2) involving in situ formed N-rich heterocyclic ligand L2 at 80 °C; two complexes of [Zn2(cis-L2)X4] (S = H2O for 3, S = 0 for 5) involving in situ formed azaheterocyclic ligand cis-L2 at 100 °C; and the rest two ones of [[Zn2(trans-L2)]S4] (4 and 6) involving in situ formed azaheterocyclic ligand trans-L2 at 120 °C (where X = Cl (1, 3, 4) and N2 (2, 5, 6), L1 = N-[2-pyridymethyl]-pyridine-2-carbaldimine, L2 = 1-pyridineimidazo-[1,5-a]pyridine, L3 = 1-(2,2-dilpyridyl-2-yI)-2-[(3-pyridin-2-yl)imidazo-[1,5-a]-pyridin-1-yl-ethyl]-3-(pyridin-2-yl)H-imidazo-[1,5-a]pyridine). Interestingly, three Cl-based complexes 1, 3, 4 under appropriate conditions can be irreversibly translated into the corresponding N2-based 2, 5, 6, respectively. The possible formation/conversion mechanism shows that the α-H activation in –CH=–N–CH2– moiety of L1 coordinated to Zn2+ 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=–N–CH2– is activated after the imino nitrogen atom is coordinated to a metal center.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=–N–C– can be represented as X=–Y=–Z of allylic type.2 Schiff base N-[2-pyridymethyl]-pyridine-2-carbaldimine (L1) 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)piprazine/pyrrole4 as well as cadmium(II) complexes with 2,2′,2″-(1-(pyridin-2-ylmethyl)imidazolodine-2,4,5-triytripyrrole4 as typical examples of such products.

Obviously, 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.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.6 (iv) Their transition-metal complexes have been also extensively used for applications in OLEDs, luminescent materials,7 etc. Hence, it is very meaningful to explore the formation conditions and coordination behaviors of multi-substituted N-rich heterocycles by solvothermal in situ metal-induced reaction from simple Schiff base ligands. Herein we report the syntheses and their subsequent coordination.
To the best of our knowledge, this is the first example that Zn\(^{2+}\)-mediated C-N bond forming strategy toward bis/tetra-imidazo[1,5-a]pyridin-2,3-yl-phenyl-based azaheterocycles can result in the formation of six temperature-dependent Zn\(^{2+}\)-complexes containing in situ formed azaheterocycles L\(^{2-}\)/L\(^{3-}\).

### Experimental section

#### Materials and methods

All reagents 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 2400C elemental analyzer. IR spectra were recorded on a Nicolet FT-IR-170SX spectro-photometer in KBr pellets. Thermogravimetric analyses were performed on a Jeol JMS-700A spectrometer at a heating rate of 10 °C min\(^{-1}\) in flowing air atmosphere. The solid state luminescent spectra were recorded around room temperature on Hitachi F-2500 and Edinburgh FLX-900 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 tube and a graphite monochromator.

Nitrogen and hydrogen adsorption isotherms were taken on a Belsorp-Max surface area and pore size analyzer.

### Synthesis of L\(^{1}\)

For complexes 1–6, they were prepared by a similar procedure except reaction temperature and auxiliary ligand Na\(_3\)N. A mixture of N-(2-pyridylmethyl)pyridin-2-carboxaldehyde (L\(^{1}\)) (0.0394 g, 0.2 mmol), ZnCl\(_2\) (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 Na\(_3\)N (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 Et\(_2\)O (2 × 3 mL), and dried in air (Table 1).

### Syntheses of complexes 1–6

Zn\(^{2+}\)Cl\(_2\) (1). Yield: 75% (based on Zn). Elemental analysis (calcd (%) for C\(_{18}\)H\(_{14}\)ZnCl\(_2\)N\(_4\): 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 (w), 1419 (s), 1376 (w), 1340 (m), 1252 (w), 1171 (m), 1073 (w), 1002 (w), 847 (w), 782 (m), 763 (w), 673 (w), 653 (w), 519 (w), 467 (w).

Zn\(^{2+}\)Cl\(_2\)\((N_3)_{2}\) (2). Yield: 69% (based on Zn). Elemental analysis (calcd (%) for C\(_{18}\)H\(_{14}\)ZnCl\(_2\)N\(_8\): C, 49.57; H, 3.21; N, 32.13. Found: C, 49.59; H, 3.24; N, 32.09. IR frequencies (KBr, cm\(^{-1}\)): 3563-3446 (br, s), 2959 (w), 2798 (m), 2063 (m), 1635 (s), 1574 (s), 1421 (s), 1335 (s), 1259 (w), 1193 (w), 1154 (m), 1006 (m), 923 (m), 879 (w), 777 (s), 646 (w), 620 (m), 564 (w), 515 (s).

Zn\(^{2+}\)Cl\(_4\)\(\cdot\)H\(_2\)O (3). Yield 75% (based on Zn). Elemental analysis (calcd (%) for C\(_{36}\)H\(_{26}\)Zn\(_2\)Cl\(_4\)N\(_8\)O: C, 50.16; H, 3.25; N, 13.01. Found: C, 50.18; H, 3.27; N, 13.05. IR frequencies (KBr, cm\(^{-1}\)): 3561-3433 (br, s), 2955 (m), 2372 (s), 2051 (m), 1639 (s), 1574 (s), 1421 (s), 1335 (s), 1259 (w), 1193 (w), 1154 (m), 1006 (m), 923 (w), 879 (w), 777 (s), 664 (w), 620 (m), 564 (w), 515 (m).

Zn\(^{2+}\)\((\text{cis-L})\)Cl\(_2\)\(\cdot\)H\(_2\)O (4). Yield 67% (based on Zn). Elemental analysis (calcd (%) for C\(_{36}\)H\(_{26}\)Zn\(_2\)Cl\(_4\)N\(_8\): C, 50.16; H, 3.25; N, 13.01. Found: C, 50.18; H, 3.27; N, 13.05. IR frequencies (KBr, cm\(^{-1}\)): 3561-3432 (br, s), 2955 (m), 2372 (s), 2051 (m), 1639 (s), 1574 (s), 1421 (s), 1335 (s), 1259 (w), 1193 (w), 1154 (m), 1006 (m), 923 (w), 879 (w), 777 (s), 646 (w), 620 (m), 564 (w), 515 (m).

Zn\(^{2+}\)\((\text{cis-L})\)Cl\(_4\)\(\cdot\)H\(_2\)O (5). Yield 73% (based on Zn). Elemental analysis (calcd (%) for C\(_{36}\)H\(_{26}\)Zn\(_2\)Cl\(_4\)N\(_8\): C, 50.16; H, 3.25; N, 13.01. Found: C, 50.18; H, 3.27; N, 13.05. IR frequencies (KBr, cm\(^{-1}\)): 3565-3443 (br, s), 2994 (m), 2878 (m), 2796 (m), 2045 (m), 1634 (s), 1589 (s), 1534 (s), 1471 (s), 1444 (m), 1347 (m), 1290 (s), 1187 (s), 1150 (s), 1023 (s), 902 (s), 794 (m), 764 (m), 678 (m), 635 (m), 603 (m), 574 (w), 525 (w), 464 (w).

Zn\(^{2+}\)\((\text{trans-L})\)\(\cdot\)H\(_2\)O (6). Yield 70% (based on Zn). Elemental analysis (calcd (%) for C\(_{36}\)H\(_{26}\)Zn\(_2\)Cl\(_4\)N\(_8\): C, 50.16; H, 3.25; N, 13.01. Found: C, 50.18; H, 3.27; N, 13.05. 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).

Zn\(^{2+}\)\((\text{trans-L})\)\(\cdot\)H\(_2\)O (7). Yield 70% (based on Zn). Elemental analysis (calcd (%) for C\(_{36}\)H\(_{26}\)Zn\(_2\)Cl\(_4\)N\(_8\): C, 50.16; H, 3.25; N, 13.01. Found: C, 50.18; H, 3.27; N, 13.05. IR frequencies (KBr, cm\(^{-1}\)): 3566-3446 (br, s), 2996 (m), 2893 (m), 2798 (s), 2061 (m), 1636 (s), 1574 (s), 1471 (s), 1433 (s), 1341 (s), 1259 (w), 1151 (m), 1023 (s), 902 (s), 794 (m), 764 (m), 678 (m), 635 (m), 603 (m), 574 (w), 525 (w), 464 (w).
Table 1  Crystallographic data and structure refinement summary for 1–6

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* R₁ = ∑||F₁| − |F₂||/∑|F₁|, wR₂ = {∑(w(F₁) − F₂)²)/∑F₁²}¹/², where w = 1/(a²F₁ + (aP)² + bP), P = (F₁² + 2F₂²)³/³.

1598(vs), 1543(s), 1474(s), 1450(s), 1342(vs), 1295(s), 1193(vs), 1153(m), 1026(s), 897(vs), 796(m), 764(s), 680(m), 644(m), 599(m), 566(m), 529(m), 468(w).

Alternatively, two N₃-based complexes 5, 6 can be also obtained via stirring reactions from NaN₃ 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 monochromatized Mo-Kα radiation (λ = 0.71073 Å). Absorption corrections were applied using the multiple-scan program SADABS. Structural solutions and full-matrix least-squares refinements based on F² 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 0.96 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 is 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.

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 (L¹) with ZnCl₂/ZnCl₂ + NaN₃ in the mixed solvents of DMF and pyridine (ν/ν = 2 : 1) at 80–120 °C for three days (see Scheme 1). The component diversification of the resulting discrete Zn²⁺⁻L₁⁻⁻⁻ complexes 1–6 can be tuned simply by changing reaction temperature, in which in situ forming L²⁻⁻⁻ / L³⁻⁻⁻ are the results of intermolecular C⁻⁻⁻C⁻⁻⁻⁻N coupling and ring-forming reactions deriving from z-H activation at ortho-position of imine –CH⁻⁻⁻⁻N–CH⁻⁻⁻⁻– moiety reduced by Zn(II) coordination (possible in situ forming mechanism in Scheme S1†). Elemental analysis and PXRD (Fig. S1 in the ES†) 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 NaN₃ and the Cl-based complexes 1, 3 and 4 for 5 hours at 100 °C and 120 °C can irreversibly convert into corresponding N₃-based complexes 5 and 6 in high yield, respectively. Or alternatively the direct reaction of L₁ with ZnCl₂ + NaN₃ like the Cl-based complexes 1, 3 and 4 can also give the corresponding N₃-based complexes 2, 5 and 6. However, they are not only low yield, but also difficult to isolate and purify. This probably stems from the diverse coordination modes of azide anion (such as η⁻⁻⁻¹, μ(1,1)- and μ(1,3)-modes, etc.), especially under high temperature conditions. In contrast, azide substitution reactions based on Cl-based zinc complexes, due to a single final product, have obvious advantages.

In the IR spectra of six compounds 1–6, the strong bands in the region of 3443–3567 cm⁻¹ or so are due to a hydrogen bonding C–H···Cl(N) interactions. The strong C–N bands occurring in the range of 1597–1635 cm⁻¹ for these complexes are shifted considerably toward lower frequencies compared to that of the free Schiff base ligand L₁ (1646 cm⁻¹), showing that the azomethine nitrogen atom is coordinated to the metal. The weak bands in the region of 462–467 cm⁻¹ for the six complexes can be assigned to ν(M–N/Cl), and provides further evidence for the coordination was through the terminal nitrogen/chlorine atoms. The position of the 2061–2063 cm⁻¹ (rᵗw-N₃) falls within the absorption range of terminal azides in

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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 \( \text{ZnCl}_2 \) at 80 °C lasted for three days, 0-D compound 1 was obtained. Its asymmetric unit involves one crystallographically independent mononuclear molecule \( \text{ZnL}_2\text{Cl}_2 \) (Fig. 1), and each molecule has a basically undistorted square pyramidal coordination geometry around the zinc(II) ion satisfied by three nitrogen atoms (N1, N2, N3) from \( \text{in situ} \) formed ligand \( L^2 \) and two terminal coordinated chlorine atoms (Cl1, Cl2). The Zn–N bond length of \( (2.030(4) - 2.385(4) \text{ Å}) \), and Zn–Cl \( (2.2602(14) - 2.2626(16) \text{ Å}) \) 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 π···π packing interactions (Table S3†), a 2-D supramolecular layer-like structure with 4\(^4\) topology is assembled and as indicated in Fig. 2.

\( \text{ZnL}_2^2(\text{N}_3)^2 \) (2). When \( \text{NaN}_3 \) is added to the reaction mixture, two coordinated chlorine atoms in 1 are replaced by two azide ions and produce a new complex \( \text{ZnL}_2^2(\text{N}_3)^2 \) (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

Fig. 1 Molecular structure of compound \( \text{ZnL}_2\text{Cl}_2 \) (1) with atomic labels.

Fig. 2 In 1, (a) 2-D supramolecular layer assembled by intermolecular hydrogen bonding C–H···Cl (blue color) and π···π packing (violet color) interactions in bc plane. (b) 4\(^4\) topological supramolecular layer, in which the dimmer unit \( \text{ZnL}_2\text{Cl}_2 \) as node constructed by intermolecular C–H···Cl and π···π packing interactions, interunit hydrogen bond C–H···Cl as linker.

Fig. 3 Molecular structure of \( \text{ZnL}_2^2(\text{N}_3)^2 \) (2) with atomic labels.

\( \text{Zn}^{2+} \) ion, one \( \text{in situ} \) 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 \( L^2 \) coordinate to one \( \text{Zn}^{2+} \) 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 π···π stacking interactions (Table S3†) resulting in 3-D supramolecular network with \( 3^3\times13 \cdot 5^6\cdot6^5 \) topology further stabilize crystal structure (Fig. 4).

\( \text{Zn}_3(\text{cis-L}^3)^2\text{X}_4, S \) (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 \( \text{in situ} \)
formed ring-forming and C–C coupling product L3 from ligand L2 and 2-pyridine formaldehyde were obtained as the two isologues. Both compounds 3 and 5 are 0-D dinuclear structures with monoclinic P2(1)/c space group.

As shown in Fig. 5, the molecule of 3 with a C2 rotary axis contains two Zn(n) ions, one in situ formed ligand L3, four terminal Cl− ions and one lattice water molecule. Zn1 atom is penta-coordinated by three nitrogen atoms (N1, N2, N4) from the same ligand L3 and two terminal chloride atoms (Cl1, Cl2) and presents a slightly distorted trigonal bipyrimidal coordination geometry. The ligand L3, which adopts cis-conformation of four coordinated terminal groups referred to C6–C6a single bond and coordinates to two Zn2+ ions, shows μ3-η1:η1:η1:η1:η1 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†) makes dinuclear molecular unit Zn2(cis-L3)Cl4 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− ion, azide may have different spatial orientation, however compound 5 presents the same P2(1)/c space group. The molecule of 5 consists of two crystallographically independent Zn(n) ions showing a slightly distorted trigonal bipyrimidal coordination geometry, one in situ formed ligand L3 with μ3-η1:η1:η1:η1:η1 coordination mode and four terminal η1-N3− 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 Zn2(cis-L3)(N3)4 links seven adjacent units to assemble into 3-D supramolecular network. If the dinuclear molecular unit Zn2(cis-L3)(N3)4 viewed as the node and the hydrogen bonding C–H···N interactions (Table S3†) as the linker, the resulting network can be simplified as 33·410·56·62 topology as displayed in Fig. 8.

[[Zn2(trans-L3)X4]. (X = Cl for 4 and X = N3 for 6). When the reaction temperature finally rising to 120 °C, two complexes 4

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**Formed Ring-Forming and C–C Coupling Product L3 from Ligand L2 and 2-Pyridine Formaldehyde**

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**Fig. 4** 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 36·410·56·62 topology.

**Fig. 5** Molecular structure of compound Zn2(cis-L3)Cl4·H2O (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** 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 L₃ were formed as the two isologues. Both compounds 4 and 6 are 0-D dinuclear structures with monoclinic P2(1)/n space group for 4 and P1 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 pentacoordinated by three nitrogen atoms (N1, N2, N4) from the ligand L³ and two terminal chloride atoms (Cl1, Cl2), demonstrating trigonal bipyramidal coordination geometry similar to that of its conformational isomer 3. One ligand L¹, which is trans-conformation of four coordinated terminal groups referred to C6–C6a bond, coordinates to 2 equiv. of Zn²⁺ ions showing μₜ⁻η¹⁻η¹⁻η¹⁻η¹⁻η¹ coordination mode. Meanwhile, the existence of intermolecular hydrogen bonding C–H···Cl interactions (Table S3†) makes dinuclear molecular [Zn₂(trans-L³)Cl₄] unit to be assembled into a 3-D supramolecular network with the topology of 3₀,₄₁₈,₆₅ as shown in Fig. 10 and 11.

When Cl⁻ 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\(^4\)-4\(^\pm\)6\(^2\) 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 L\(^1\) with a donor set of N\(_3\) was firstly applied in the system of Zn-based aza-heterocyclic complexes. Initial reaction of ZnCl\(_2\) at 80 °C with L\(^1\) together with 2-pyridine formaldehyde afforded Zn-mono-nuclear compound ZnL\(^2\)Cl\(_2\) (1) containing one in situ formed N-rich heterocycle L\(^2\) with a donor set of N\(_3\) 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 N\(_3\)\(^-\) anions and produced the corresponding mononuclear zinc(II) compound ZnL\(^2\)[N\(_3\)]\(_2\) (2). Increasing the reaction temperature to 100 °C, Zn\(^{2+}\)-induced intermolecular C–C coupling reaction between two L\(^2\) molecules resulted in the formation of cis-conformation L\(^3\) and the corresponding Cl-based compound [Zn\(_2\)(cis-L\(^3\))Cl\(_4\)] (3) as well as N\(_1\)-based substitute [Zn\(_2\)(cis-L\(^3\))[N\(_3\)]\(_4\) (5). Continuing to increase the reaction temperature to 120 °C, in situ formed cis-L\(^3\) can be lightly converted to the trans-L\(^3\) and the corresponding Cl-based compound Zn\(_2\)(trans-L\(^3\))Cl\(_4\) (4) as well as N\(_1\)-based substitute [Zn\(_2\)(trans-L\(^3\))[N\(_3\)]\(_4\)] (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 L\(^2\)–\(^3\) 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 L\(^1\) can be markedly activated by the coordination induction of Zn\(^{2+}\) ion,\(^1\)\(^2\) and pyridine as basic acceptor has the ability to deprotonate the imino carbon-bound a-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 L\(^2\)/L\(^3\)–Zn (Scheme S1†).

**Fluorescence/UV absorption spectra and titration of L\(^1\) + 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).\(^2\) Meanwhile, the fluorescence response of receptor L\(^1\) towards Zn\(^{2+}\) 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, L\(^1\) 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.\(^1\)\(^4\) As stepwise addition of ZnCl\(_2\) solution in DMF at 80 °C with...
compounds of interaction.

As the temperature of the mixture [ZnCl$_2$ + L$_1$ + 2-Pfd] increased from 80 °C to 100 °C and 120 °C, the emission peak wavelength of the mixture ZnCl$_2$ + L$_1$ + 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-compounds 1, 3 and 4 was examined by fluorescence titration of 1/3/4 + NaN$_3$ at 80, 100 °C and 120 °C, respectively (Fig. 14 and S8 and S9†). The fluorescence intensity of 1/3/4 + NaN$_3$ was, to some extent, enhanced with almost unchanged peak shape and position compared to the corresponding Cl-based Zn-compounds, in which the further enhanced fluorescence intensity of NaN$_3$-based Zn-compounds 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 (L$^2$-3) containing imidazo-[1,5-a]-pyridine core involving solvothermal in situ ligand generation from simple tridentate N$_3$-set pyridine-type Schiff base ligand (L$^1$) mediated by Zn$^{2+}$. Further studies on in situ formation and conversion of ligands L$^1$-3 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 z-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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