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# Syntheses, structures and catalytic coupling reactions of two tetrazolate-based coordination polymers

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ABSTRACT

Reactions of 5-(4-nitrophenyl)-1*H*-tetrazole (H(4-nptz)) and 5-(4-nitrobenzyl)-1*H*-tetrazole (H(4-nbtz)) with transition metals under solvothermal conditions yield two new coordination polymers, namely, $[Cu^{I}(4\text{-nptz})(CH_3CN)]_n$ (**1**) and $[Zn(4\text{-nbtz})_2]_n$ (**2**). Both of them were characterized by IR, thermogravimetric analysis, X-ray crystallography. Single crystal X-ray diffraction analysis reveals that **1** is of three-dimensional (3D) *sqc184* type supramolecular framework, while **2** is of 3D *sqc1* type supramolecular framework. In addition, solid state UV–Vis diffuse reflectance and photoluminescence properties of **1** and **2** are investigated. Furthermore, the catalytic properties for the coupling reaction of α-amino acids and bromobenzene were also investigated.

## 1. Introduction

Recently, the formation of metal–organic coordination polymers (CPs) with intriguing structural topologies has attracted much attention owing to their potential functions, such as ion exchange, molecular adsorption, fluorescence, electrical conductivity, magnetism, gas storage and optical properties [1–8]. Although architectural design of coordination polymers is very popular, but the design of prospective multifunctional structures still remains a big challenge, especially the attempt to figure out the factors that influence their formation and understand the roles of different factors in the assembly [9–13]. It is well known that the final structures of such complexes can often be improved by the judicious selection of organic ligands with suitable shape, functionality, flexibility, symmetry, and the coordination geometry and nature of the metal ions, the reaction conditions, and so on [14–19]. Much attention has been focusing on tuning the coordination polymers through rational selection of structurally related ligands, such as multidentate nitrogen donor ligands, semi-rigid nitrogen donor ligands, flexible dithioether and disulfoxide ligands, benzenedicarboxylate ligands and so on [20–23].

Azole heterocycles ligands, such as pyrazole, imidazole, triazole and tetrazole which make coordination chemistry of five-membered nitrogen donor ligands more abundant and complicated, have attracted considerable interests of chemists to study their transition metal complexes [24–26]. As the derivative of azole heterocycles, 5-substituted tetrazoles have been shown to be good organic linkers in the construction of structurally versatile metal–organic coordination polymers due to their flexible coordination modes through the four nitrogen electron-donating atoms served as either a multidentate or a bridging building block in supramolecular assemblies (Scheme 1) [27] with intriguing biological, optical, magnetic and hydrogen storage properties [28–30].

In this present paper, as a part of an ongoing program in our laboratory to explore the scope of functional structure with tetrazole ligands under solvo/hydrothermal conditions [31], we report herein the synthesis and structural characterization of two structurally related tetrazole coordination polymers, namely $[Cu^{I}(4\text{-nptz})(CH_3CN)]_n$ (**1**) [H(4-nptz) = 5-(4-nitrophenyl)-1*H*-tetrazole] and $[Zn(4\text{-nbtz})_2]_n$ (**2**) [H(4-nbtz) = 5-(4-nitrobenzyl)-1*H*-tetrazole]. Complex **1** was obtained by direct reaction of 4-nptz and CuCl under solvothermal conditions, whereas complex **2** was synthesized by the *in situ* [3+2] cycloaddition reaction of 4-nitrophenylacetonitrile, sodium azide and $Zn(NO_3)_2$ through solvothermal method. The complexes have been characterized by single crystal diffraction, XRD, IR spectroscopy, TGA, elemental analysis and molar conductivity measurements. The catalytic property of complex **1** for coupling reaction of bromobenzene with α-amino acids is also investigated.

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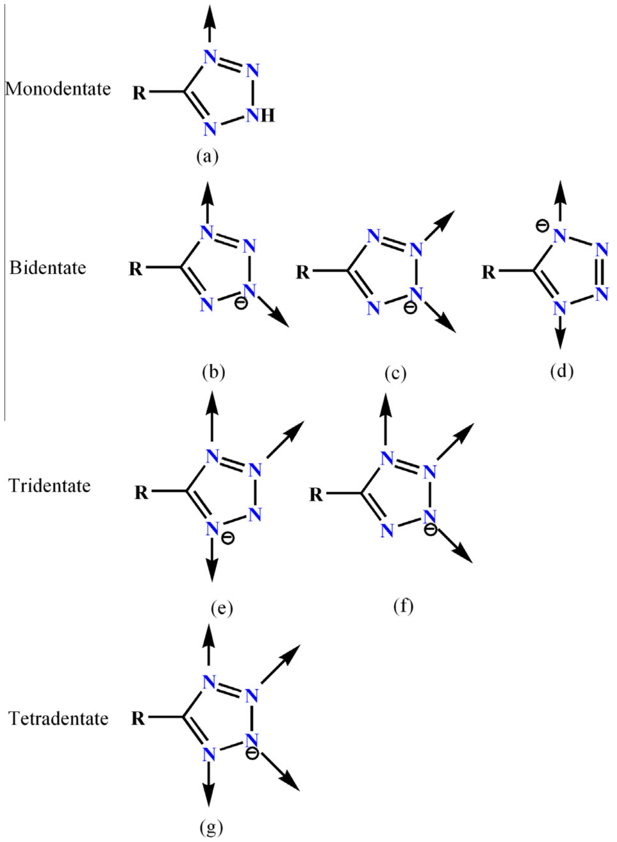


**Scheme 1.** Coordination modes of 5-substituted tetrazoles.

## 2. Experimental

### 2.1. Materials and general methods

All solvents and reagents for syntheses were commercially available and used without further purification. $^1H$ NMR spectra were recorded on a Bruker Avance (400 MHz) spectrometer in DMSO with TMS as standard. IR spectra were recorded on a PerkinElmer precisely Spectrum 100 apparatus in the region of 450–4000 $cm^{-1}$. The dry sample powder is mixed by KBr and treated directly in the purpose-made IR cell. Elemental analyses were performed on a Perkin-Elmer-2400 Series II analyzer. The UV–Vis diffuse reflectance spectra were carried out for their solid states, with using a Cary 5000 UV–Vis-NIR analyzer. Thermogravimetric measurements were done on a Perkin-Elmer TGA 7 analyzer in the temperature range of 25–800 °C in $N_2$ atmosphere at a heating rate of 10 °C $min^{-1}$. X-ray powder diffraction measurement, whose range of $2\theta$ is from 5° to 50°, was performed on a Rigaku D/Max–IIIB X-ray diffractometer Cu Kα ($\lambda = 1.5406$ Å) radiation (40 kV and 200 mA) and Ni filter.

### 2.2. Syntheses of ligand 5-(4-nitrophenyl)-1H-tetrazole (H(4-nptz))

A mixture of 4-nitrobenzonitrile (7.4 g, 0.05 mol) in DMF (120 mL), sodium azide (5.2 g, 0.08 mol) and $NH_4Cl$ (4.28 g, 0.08 mol) were refluxed for 20 h, yellow precipitate of ligand H(4-nptz) was then filtered off after cooling and dried under vacuum with a yield of 53%. *Anal.* (wt%) Calc. for $C_7H_5N_5O_2$: C, 43.98; H, 2.64; N, 36.64. Found: C, 43.97; H, 2.64; N, 36.65%. IR (KBr, $cm^{-1}$): 3207 (m), 3102 (m), 1605 (m), 1552 (m), 1515 (s), 1339 (s), 1109 (w), 1065 (m), 998 (w), 861 (m), 774 (w), 729 (m), 498 (m).

### 2.3. Syntheses of ligand 5-(4-nitrobenzyl)-1H-tetrazole (H(4-nbtz))

The synthesis of ligand 5-(4-nitrobenzyl)-1*H*-tetrazole was similar to that of H(4-nptz) except that aqueous solution (100 mL) of 4-nitrophenylacetonitrile (5.6 g, 0.034 mol) being used instead of 4-nitrobenzonitrile in DMF. After cooled and dried under vacuum, red precipitate of ligand H(4-nbtz) was obtained with a yield of 41%. *Anal.* (wt%) Calc. for $C_8H_7N_5O_2$: C, 46.79; H, 3.41; N, 34.12. Found: C, 46.79; H, 3.42; N, 3.41%. IR (KBr, $cm^{-1}$): 3113 (w), 2945 (w), 2250 (w), 1945 (w), 1600 (m), 1513 (s), 1345 (s), 1109 (m), 1012 (w), 922 (w), 832 (m), 735 (m), 465 (w).

### 2.4. Syntheses of complex **1**

CuCl (0.1 g, 1 mmol), H(4-nptz) (0.095 g, 0.5 mmol), $H_2O$ (7 mL) and $CH_3CN$ (3 mL) were mixed in a 15 mL Teflon-lined stainless-steel vessel and stirred for 30 min, which was then put into an oven at 130 °C and kept for 72 h. Then the oven was slowly cooled to room temperature with a rate of 5 °C/h. After washed thoroughly with absolute ethyl alcohol, yellow crystals were obtained in 29% yield (based on the ligand). *Anal.* (wt%) Calc. for $C_9H_7CuN_6O_2$: C, 36.64; H, 2.37; N, 28.50. Found: C, 36.66; H, 2.38; N, 28.48%. IR (KBr, $cm^{-1}$): 3088 (w), 1940 (w), 1603 (m), 1518 (s), 1444 (m), 1339 (s), 1108 (w), 1009 (w), 855 (s), 734 (m), 692 (m), 499 (w).

### 2.5. Syntheses of complex **2**

Complex **2** was synthesized by the *in situ* [3+2] cycloaddition reaction. 4-nitrophenylacetonitrile (0.648 g, 4.3 mmol), sodium azide (0.39 g, 6 mmol), $Zn(NO_3)_{2.}$ (0.594 g, 2 mmol), $H_2O$ (9 mL) and $CH_3CH_2OH$ (1 mL) were sealed in a 15 mL Teflon-lined stainless-steel autoclave, which was heated to 120 °C and held for 3 days. After slowly cooled to room temperature at a rate of 5 °C/h, yellow transparent plate-like crystals of **2** with 52% yield were obtained. *Anal.* (wt%) Calc. for $C_{16}H_{12}N_{10}O_4Zn$: C, 40.53; H, 2.53; N, 29.55. Found: C, 40.54; H, 2.54; N, 29.53%. IR (KBr, $cm^{-1}$): 3392 (w), 3065 (w), 2129 (w), 1599 (m), 1516 (s), 1439 (m), 1391 (m), 1351 (s), 1221 (m), 1105 (m), 1068 (m), 860 (m), 735 (s), 527 (w), 399 (m).

### 2.6. X-ray crystallographic determination

The suitable samples of size 0.21 mm × 0.16 mm × 0.15 mm for **1** and 0.23 mm × 0.20 mm × 0.10 mm for **2** were chosen for the crystallographic study and then mounted on a BRUKER SMART APEX CCD diffractometer with $\omega$-scan mode in the range of $3.15° < \theta < 30.01°$ for **1** and $3.13° < \theta < 27.48°$ for **2**, respectively. All diffraction measurements were performed at room temperature using Mo Kα radiation ($k = 0.71073$ Å). For **1**, a total of 5477 (2909 independent, $R_{int} = 0.0328$) reflections were measured. For **2**, a total of 8700 (3782 independent, $R_{int} = 0.0292$) reflections were measured. The structures were solved using direct method and refined by full-matrix least-squares methods on $F^2$ by using SHELX-97 program package [32]. All non-hydrogen atoms are found from the different Fourier maps and refined anisotropically. And the hydrogen atoms are placed in calculated positions and treated as riding on their parent atoms. A summary of the crystallographic data and structure refinement parameters for **1** and **2** are given in Table 1. Selected bond lengths for **1** and **2** are given in Table 2.

### 2.7. Complex **1** catalyzed coupling reaction of bromobenzene with α-amino acid

A Schlenk tube was charged with amino acid (3.2 mmol), bromobenzene (3.2 mmol), $K_2CO_3$ (4.8 mmol) and complex **1**

**Table 1**
Crystal data and structure refinements for complexes **1** and **2**.

| Crystal parameters | **1** | **2** |
|---|---|---|
| CCDC No. | 1034547 | 1034548 |
| Formula | $C_9H_7CuN_6O_2$ | $C_{16}H_{12}N_{10}O_4Zn$ |
| Formula weight | 294.75 | 473.73 |
| Space group | $P2_1/c$ | $Pc$ |
| $a$ (Å) | 12.2891(5) | 5.5263(11) |
| $b$ (Å) | 10.3566(4) | 17.491(4) |
| $c$ (Å) | 9.3372(3) | 9.7331(19) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 105.211(4) | 92.05(3) |
| $\gamma$ (°) | 90 | 90 |
| $V$ (Å$^3$) | 1146.74(7) | 940.2(3) |
| $Z$ | 4 | 2 |
| $D_{calc.}$ (g cm$^{-3}$) | 1.707 | 1.673 |
| $\mu$ (mm$^{-1}$) | 1.908 | 1.357 |
| $F(000)$ | 592 | 480 |
| $R_{int}$ | 0.0328 | 0.0292 |
| Goodness-of-fit (GOF) on $F^2$ | 1.109 | 1.069 |
| $R_1$, $wR_2$ ($I > 2\sigma(I)$) | 0.0494, 0.0969 | 0.0291, 0.0658 |
| $R_1$, $wR_2$ (all data) | 0.0796, 0.1091 | 0.0314, 0.0702 |

**Table 2**
Selected bonds lengths (Å) and angles (°) for complexes **1** and **2**.

| Bonds (Å) | **1** | Bonds (Å) | **2** |
|---|---|---|---|
| Cu(1)–N(1) | 2.010(3) | Zn(1)–N(1) | 1.988(3) |
| Cu(1)–N(6) | 2.026(3) | Zn(1)–N(4)$^{I}$ | 2.022(3) |
| Cu(1)–N(2)$^{I}$ | 2.027(3) | Zn(1)–N(6) | 1.989(3) |
| Cu(1)–N(4)$^{II}$ | 2.082(3) | Zn(1)–N(8)$^{II}$ | 1.987(3) |
| Bond angles (°) | **1** | Bond angles (°) | **2** |
| N(1)–Cu(1)–N(6) | 114.3(1) | N(8)$^{II}$–Zn(1)–N(1) | 114.6(2) |
| N(1)–Cu(1)–N(2)$^{I}$ | 111.9(1) | N(8)$^{II}$–Zn(1)–N(6) | 118.5(2) |
| N(6)–Cu(1)–N(2)$^{I}$ | 112.1(1) | N(1)–Zn(1)–N(6) | 105.8(2) |
| N(1)–Cu(1)–N(4)$^{II}$ | 111.1(1) | N(8)$^{II}$–Zn(1)–N(4)$^{I}$ | 107.9(1) |
| N(6)–Cu(1)–N(4)$^{II}$ | 98.5(1) | N(1)–Zn(1)–N(4)$^{I}$ | 105.5(1) |
| N(2)$^{I}$–Cu(1)–N(4)$^{II}$ | 108.0(1) | N(6)–Zn(1)–N(4)$^{I}$ | 103.3(1) |

Symmetry code: **1**, I: $-x + 2, -y + 1, -z$; II: $-x + 2, y + 1/2, -z + 1/2$. **2**, I: $x, -y + 2, z - 1/2$; II: $x + 1, y, z$.

(0.32 mmol). Under $N_2$ atmosphere, DMA (4 mL) was added by syringe. The tube was sealed and heated at 90 °C for 48 h. After cooled to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate and 5 mL of water. Concentrated HCl was then added to adjust the pH to 3. The organic layer was separated and the aqueous layer extracted with ethyl acetate (5 × 20 mL). The combined organic layers were washed with brine, dried over $Na_2SO_4$ and concentrated by rotavapor. The residual oil was loaded on a silica gel column and eluted with ethyl acetate/petroleum ether (1/5 to 1/1) to afford the final coupling product.

*N-phenyl-L-valine (1):* 83% yield; $^1$H NMR (400 MHz, DMSO) $\delta$ ppm: 7.07 (t, $J = 7.78$ Hz, 2H), 6.49–6.70 (m, 1H), 5.66 (br. s, 2H), 3.64 (d, $J = 6.78$ Hz, 1H), 1.94–2.15 (m, 1H), 0.79–1.21 (m, 6H); *Anal.* Calc. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.24. Found: C, 68.35; H, 7.75, N, 7.12%.

*N-phenyl-L-phenylalanine (2):* 91% yield; $^1$H NMR (400 MHz, DMSO) $\delta$ ppm: 7.17–7.37 (m, 2H), 7.06 (t, $J = 7.65$ Hz, 1H), 6.59 (d, $J = 8.03$ Hz, 2H), 5.92 (br. s, 1H), 4.13 (t, $J = 6.78$ Hz, 2H), 2.91–3.16 (m, 4H); *Anal.* Calc. for $C_{15}H_{15}NO_2$: C,74.70; H, 6.22; N, 5.81. Found: C, 74.49; H, 6.32, N, 5.73%.

*N-phenyl-L-tyrosine (3):* 65% yield; $^1$H NMR (400 MHz, DMSO) $\delta$ ppm: 7.00–7.13 (m, 4H), 6.66 (d, $J = 8.53$ Hz, 2H), 6.67 (d, $J = 7.15$ Hz, 2H), 6.56 (m, 1H), 5.82 (t, $J = 7.6$ Hz, 1H), 3.97–4.10 (m, 1H), 2.81–3.01 (m, 1H); *Anal.* Calc. for $C_{15}H_{15}NO_3$: C, 70.03; H, 5.88; N, 5.44. Found: C, 70.06; H, 5.82; N, 5.36%.

*N-phenyl-L-alanine (4):* 72% yield; $^1$H NMR (400 MHz, DMSO) $\delta$ ppm: 7.07 (t, $J = 7.78$ Hz, 2H), 6.62 (t, $J = 7.4$ Hz, 1H), 6.55 (d, $J = 8.2$ Hz, 2H), 3.94 (q, $J = 6.94$ Hz, 1H), 1.38 (d, $J = 7.03$ Hz, 3H); *Anal.* Calc. for $C_9H_{11}NO_2$: C, 65.48; H, 6.67; N, 8.48. Found: C, 65.50; H, 6.77; N, 8.39%.

## 3. Results and discussion

### 3.1. Syntheses of the complexes

*Caution!* Due to the fact that sodium azide is potentially explosive and dangerous, small amount of compounds are prepared in each experiment and should be handled with extra care.

Both H(4-nptz) and H(4-nbtz) are slightly soluble in water and are difficult to coordinate with metal atom at room temperature. Since the crystalline products **1** and **2** cannot be obtained by direct aqueous reactions at room temperature, the solvo/hydrothermal technique is applied to cultivate their crystals. Notably, two completely different synthetic methods were employed to obtain crystalline products under solvothermal conditions. Complex **1** was obtained by direct reaction of 4-nptz and CuCl under solvothermal condition, whereas complex **2** was synthesized by the in *situ* [3+2] cycloaddition reaction of 4-nitrophenylacetonitrile, sodium azide and $Zn(NO_3)_2$, which skipped the synthesis of 4-nbtz. Noteworthy, we also tried to synthesize the complex **2** by direct reaction similar to that of complex **1**, however, an unknown powder were obtained as the products. In addition, complex **1** was prepared with metal ion and ligand molar ratio of 2:1, the attempt to change the molar ratio of reactants to 1:2 or other ratios still results in the same product with slightly lower yields.

### 3.2. Thermal analysis of complexes *1* and *2*

As important property of inorganic–organic hybrid materials, the thermal stabilities of complexes **1** and **2** were studied by thermogravimetric experiments conducted under air atmosphere. However, several tests show that explosion would occur to complex **1** and **2** when the temperature is higher than 325 °C for **1**, and 368 °C for **2**. Before the explosion, the acetonitrile molecule in complex **1** is lost during 160–325 °C (calculated: 13.9%; found: 14.3%) (Fig. S1, in Supporting Information).

### 3.3. Structural description of complexes *1* and *2*

Complex **1** crystallized in a monoclinic system with $P2_1/c$ space group. The asymmetric unit of **1** consists of one Cu$^{I}$ center, one 4-nptz ligand and one $CH_3CN$ molecule. The Cu$^{I}$ center is surrounded by four nitrogen atoms with slightly distorted tetrahedral geometry, in which three nitrogen atoms (N1, N2$^{I}$, N4$^{II}$) are from three 4-nptz ligands and one nitrogen atom (N6) from one acetonitrile molecule (Fig. 1a). The lengths of Cu–N bonds are in the range of 2.010(3)–2.082(3) Å with an average of 2.036 Å, and the N–Cu–N angles range from 98.5(1)° to 114.3(1)°.

In complex **1**, each 4-nptz acts as a tridentate linker (type e in Scheme 1) connecting three Cu$^{I}$ centers to form a 2D planar network paralleling to *bc* plane. This network containing two types of cavity, one is a six-membered ring with the closest Cu···Cu distance of 3.589(1) Å, another one is a sixteen-membered ring covered by nitrophenyl groups (Fig. 1b). Furthermore, TOPOS program [33] indicates that this 2D plane can be reduced to a 3-connected *fes* type topology with a point symbol of (4·8$^2$). These *fes* type network are pillared by nitrophenyl groups and linked by C–H···O hydrogen bonding interactions between the methyl groups of the acetonitrile and the nitro groups of the adjacent planes, leading to a 3D supramolecular framework. Furthermore, when the acetonitrile molecule serves as a bridging linker and both of the 4-nptz molecule and the Cu$^{I}$ cation be seen as the four-

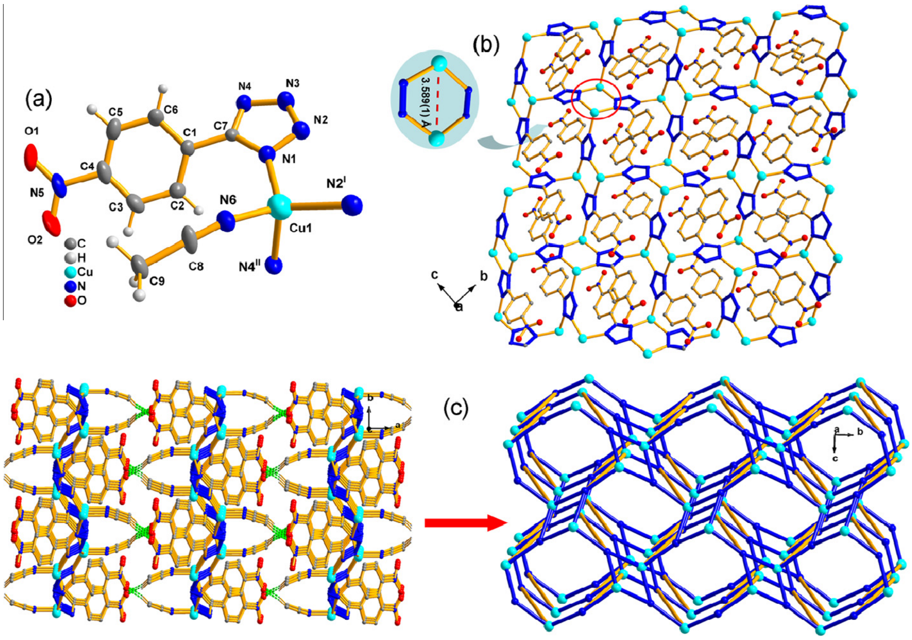


**Fig. 1.** (a) Stick-ball representation of the molecule structure of **1** with thermal ellipsoids at 50% probability; (b) View of the 2-D grid network architectures of the **1**; (c) Schematic illustration of 3D (4,4)-connected *sq c184* type topology framework with a points symbol of $(4{\cdot}6^5)$. Symmetry code: (I) $2 - x, 1 - y, -z$; (II) $2 - x, 0.5 + y, 0.5 - z$.

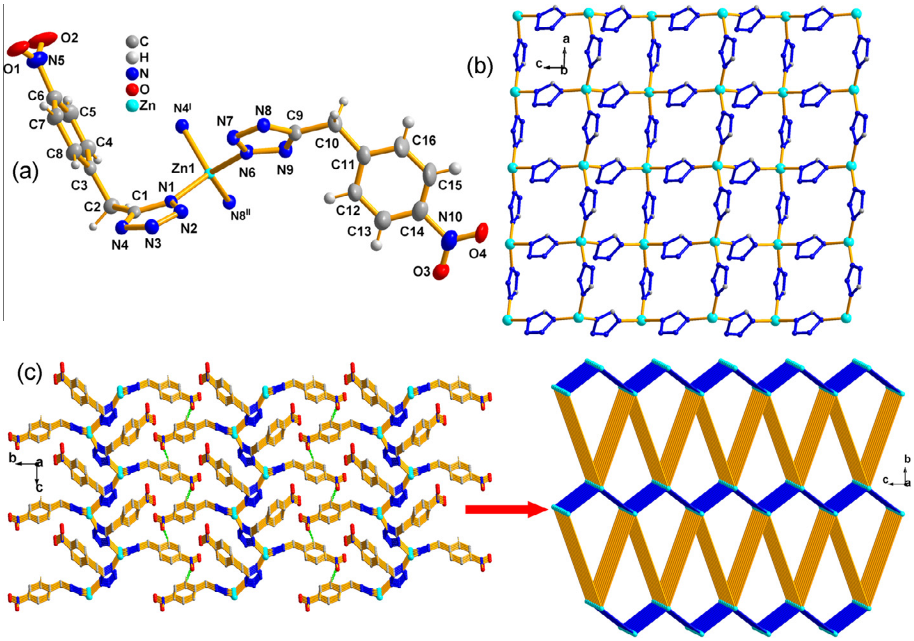


**Fig. 2.** (a) Stick-ball representation of the molecule structure of **2** with thermal ellipsoids at 50% probability; (b) View of the 2-D grid network architectures of the **2**; (c) Schematic illustration of 3D 6-connected *sqc1* type topology framework with a points symbol of $(4^{12}{\cdot}6^3)$. Symmetry code: (I) $x, 2 - y, -0.5 + z$; (II) $1 + x, y, z$.

connected node, the above framework could be reduced as a (4,4)-connected *sqc184* type 3D supramolecular framework with a point symbol of $(4{\cdot}6^5)$ (Fig. 1c).

It is interesting that when H(4-nbtz) instead of H(4-nptz) is used to synthesize complex **2**, which displays a 2D coordination network, however, a totally different 3D supramolecular structure. Single-crystal X-ray diffraction analysis shows that complex **2** crystallized in a monoclinic system with *Pc* space group. The asymmetric unit of **2** includes one $Zn^{II}$ center and two 4-nbtz ligands. The $Zn^{II}$ center also adopts a four-coordinated tetrahedral geometry defined by four nitrogen atoms ($N1, N4^I, N8^{II}, N6$) of four 4-nbtz ligands (Fig. 2a). The bonds distances and angles around $Zn^{II}$ ion are 1.988(3)–2.022(3) Å for Zn—N bonds with an average of 1.997 Å and 103.3(1)–118.5(9)° for N—Zn—N angles, which are all within the normal range generally with those found in the other reported $Zn^{II}$-tetrazole polymer [34].

Interestingly, the two 4-nbtz ligands in **2** serve as bidentate linkers, however, displaying different coordination modes (type d for $4\text{-nbtz}_{(N1N4)}$ and type b for $4\text{-nbtz}_{(N6N9)}$, in Scheme 1). The $4\text{-nbtz}_{(N1N4)}$ molecules connect the $Zn^{II}$ ions to form chains along *c* axis, which are further bridged by the 4-nbtz$_{(\mathrm{N6N9})}$ molecules along *a* axis to generate an undulated square grid network paralleling to *ac* plan (Fig. 2b), which can be reduced to a 4-connected *sq1* type topology with a point symbol of ($4^4 \cdot 6^2$). The closest Zn⋯Zn distances along *a* axis and *c* axis in square-grid structure are 5.526(1) Å and 6.139(1) Å, respectively. In comparison with complex **1**, there is no acetonitrile molecule in **2**, thus the nitro groups accept the H atoms from benzene rings to form C—H⋯O hydrogen bonds. These C—H⋯O hydrogen bonds link the adjacent undulated planes into a 3D supramolecular framework. Furthermore, when the hydrogen bonding linking the two 4-nbtz ligands are seen as a line and the $Zn^{II}$ cation as a six-connected node, the above framework could be reduced as a 6-connected *sqc1* type 3D supramolecular framework with a point symbol of ($4^{12} \cdot 6^3$) (Fig. 2c).

### 3.4. X-ray powder diffraction

To make sure the phase purity of these crystals, the X-ray powder diffraction (XRPD) measurements are performed for **1** and **2** (Fig. S2). The experimental XRPD patterns of the two polymers are quite similar to those calculated ones from their single-crystal X-ray data, indicating that the bulk products of complexes **1** and **2** are both pure phase. The intensity differences between experimental and calculated XRPD patterns are due to the variation in preferred orientation of the powder sample during collection of the experimental XRPD.

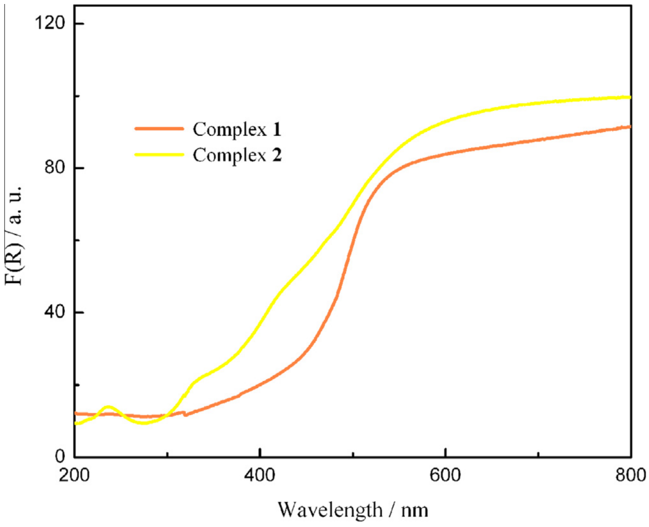


**Fig. 3.** UV–Vis diffuse reflectance spectra of complexes **1** and **2**.

### 3.5. UV–Vis diffuse reflectance spectroscopy of complexes 1 and 2

The UV–Vis diffuse reflectance spectroscopy of complexes **1** and **2** were carried out under solid states by a Cary 5000 UV–Vis-NIR analyzer. As shown in Fig. 3, the UV–Vis diffuse reflectance spectra exhibits a strong absorption band in the visible light region around 550 nm for **1** and 600 nm for **2**, which may owe to their potentially low-energy absorptions that arise from ligand-to-metal charge transfer (LMCT) [35], resulting in the yellow color of complex **1** and light-yellow color of complex **2**.

### 3.6. Photoluminescence properties of complexes 1 and 2

The photoluminescence properties of H(4-nptz) and **1**, H(4-nbtz) and **2** were investigated in the solid state at room temperature (Fig. 4). The H(4-nptz) and H(4-nbtz) molecules, respectively, exhibit emission bands at 584 and 550 nm with excitation at 390 nm. The observed emissions of H(4-nptz) and H(4-nbtz) are probably assigned to the $\pi$–$\pi^*$ transitions. In contrast to the ligand, **1** exhibits blue-shift with an emission maximum at 530 nm, while **2** exhibits an emission maximum at 545 nm. The observed emission of **1** and **2** are probably assigned to the $n$–$\pi^*$ transition of L molecules and electron transfer between ligand molecules and metal cations.

### 3.7. Complex 1 catalyzed coupling reaction of α-amino acids with bromobenzene

The formation of the carbon–nitrogen bond by the Pd/Cu-catalyzed coupling of aryl halides with amines has attracted much attention due to its wide applications [36]. Herein, we chose complex **1** and **2** to catalyze the coupling reaction of α-amino acids with bromobenzene. Heating a mixture of L-valine (1 equiv), bromobenzene (1 equiv), complex **1** (10 mol%) and $K_2CO_3$ (1.5 equiv) in DMA at 90 °C for 48 h, we could isolate the coupling product 1 in 83% yield (Scheme 2). Other solvents were also tested in this reaction. Over 80% yields were obtained when tert-butyl alcohol, DMF or NMPO as the solvents, respectively. However, much lower yields were observed if pyridine (34% yield) or water (15% yield) instead of DMA as the solvent (Table 3). In order to get the best reaction temperature, the reactions were carried out at 80, 90 and 100 °C. As shown in Fig. 5, after 48 h, the conversion of bromobenzene was 78.2%, 93.2% and 91.9%, respectively. Thus, the temperature of 90 °C and DMA as the solvent were selected for bromobenzene reacting with α-amino acids such as L-phenylalanine, L-tyrosine and L-alanine, giving the yield of 91%, 65% and 72%, respectively. However, complex **2** didn't show any catalytic activity to this coupling reaction.

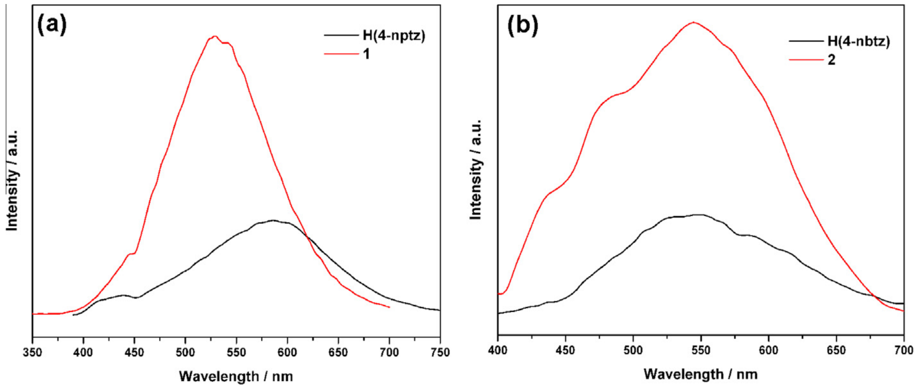


**Fig. 4.** Emission spectra of H(4-nptz) and **1**, and H(4-nbtz) and **2** in the solid states at room temperature.

**Table 3**
Complex **1** catalyzed coupling reaction of α-amino acids with bromobenzene.

| Entry | Aryl halide | Amino acid | Solvent | Product | Yield (%) |
|---|---|---|---|---|---|
| 1 | PhBr | L-valine | DMA | 1 | 83 |
| 2 | PhBr | L-valine | Tert-butyl alcohol | 1 | 80 |
| 3 | PhBr | L-valine | DMF | 1 | 82 |
| 4 | PhBr | L-valine | NMPO | 1 | 81 |
| 5 | PhBr | L-valine | Pyridine | 1 | 34 |
| 6 | PhBr | L-valine | Water | 1 | 15 |
| 7 | PhBr | L-phenylalanine | DMA | 2 | 91 |
| 8 | PhBr | L-tyrosine | DMA | 3 | 65 |
| 9 | PhBr | L-alanine | DMA | 4 | 72 |

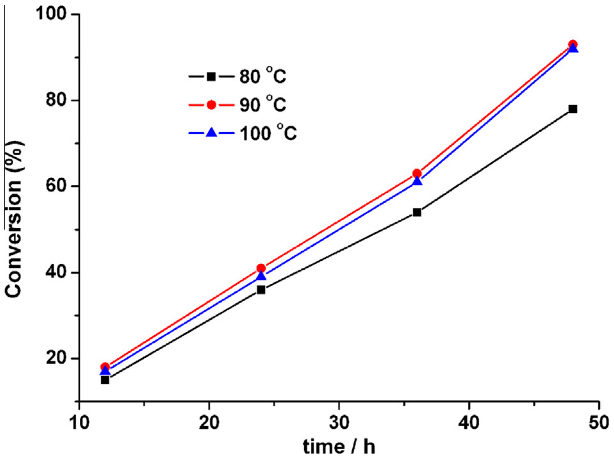
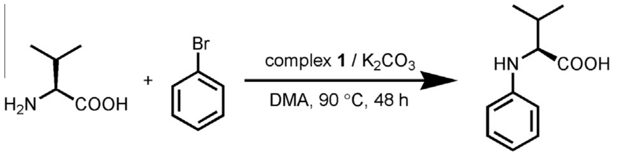


**Fig. 5.** Effect of the reaction temperature on the coupling reaction of bromobenzene with L-valine catalyzed by complex **1**.



**Scheme 2.** Complex **1** catalyzed coupling reaction of aryl halids with amino acids. Reaction conditions: 10 mol% complex **1**, 150 mol% $K_2CO_3$, PhBr (3.2 mmol), Amine (3.2 mmol), DMA (4 mL).

## 4. Conclusions

Two coordination polymers incorporating transition metals with 5-(4-nitrophenyl)-1*H*-tetrazole (4-nptz) and 5-(4-nitrobenzyl)-1*H*-tetrazole (4-nbtz) have been isolated under solvothermal conditions. Structural analyses show that the coordination modes of ligands play dominate roles on the structures of the synthesized coordination polymers. In complex **1**, the 4-nptz ligand acts as a tridentate linker, while in complex **2** the 4-nbtz ligand serves as a bidentate linker. The hydrogen bonding interactions link the 2D coordination polymers to form 3D supramolecular frameworks with *sqc184* and *sqc1* type topology, respectively. The energy transfer from the ligands to metals resulted in a strong absorption band in the visible light region around 550 nm for **1** and 600 nm for **2** in consistent with their colors. In addition, photoluminescence analysis of **1** and **2** reveals that the metal cations are able to tune the luminescent emissions of the ligands. Interestingly, the complex **1** shows catalytic property for the coupling reaction of α-amino acids and bromobenzene under relatively mild conditions, which provides an easy and economic way to synthesize some biological molecules.

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## Appendix A. Supplementary data

CCDC 1034547–48 contains the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2015.04.012.

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