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Substituted group directed assembly of zinc coordination compounds based on bifunctional ligands, from mono, di to tristetrazole-carboxylate

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Abstract: Four different tetrazole-carboxylate ligands, monotetrazole-carboxylate Hatza (Hatza=5-aminotetrazole-1-acetic acid), Hpytza (Hpytza=5-(4-pyridyl)tetrazole-2-acetic acid), ditetrazole-carboxylate H_2datza (H_2datza=N,N-di(tetrazol-5-yl)amine-N2,N2'-diacetic acid), tristetrazole-carboxylate, H_3tzpha (H_3tzpha=1,3,5-tris(tetrazol-5-yl)benzene-N2,N2',N2''-trisacetic acid) have been chosen to react with zinc salts, resulting in the formation of four novel compounds, $[Zn(atza)_2(H_2O)_4]$ (**1**), $[Zn(pytza)_2]$ (**2**), $[Zn(datza)(H_2O)_2]\cdot 3H_2O$ (**3**) and $[Zn_3(tzpha)_2(H_2O)_{12}]\cdot MeOH\cdot EtOH\cdot 4H_2O$ (**4**), whose structures are controlled by not only the number and different coordination modes of the tetrazole-carboxylate but also the complementary hydrogen bonds. These compounds have been characterized by elemental analysis, IR and single crystal X-ray diffraction. Compound **1** displays a simple zero dimensional mononuclear structure, **2** shows a classic 3D 8-connect (3^6,4^{16},5^6) tsi network topology, **3** features a 1D ladder-like chain while **4** is a 1D beaded chain. Furthermore, the luminescence properties investigated at room temperature in the solid state show excellent ligand-centered luminescence.

Keywords: Hatza/Hpytza/H_2datza/H_3tzpha; zinc; crystal structure; luminescence

Introduction

The dawn of the past decade has witnessed the prosperity of coordination compounds based on tetrazole ligands, due to not only their diversity in structure[1], but also their tunable applications in the fields of magnetism[2], ion exchange[3], catalysis[4], ferroelectric[5], absorption[6] and so on. On one hand, tetrazole-carboxylate with abundant nitrogen and oxygen atoms of the tetrazole ring and the carboxylate group, tend to display a variety of coordination modes and the -CH_2- spacer may improve the flexibility of these ligands, allowing the formation of multiple framework structures. On the other hand, it is universally acknowledged that coordination compounds based on d^{10} metals are outstanding candidates for potential application as luminescence materials, to the best of our knowledge[7]. In our previous work, some relevant compounds based on tetrazole-carboxylate ligands have been reported, such as the ones derived from tetrazole-5-carboxylate, 5-(2-pyridyl)tetrazole-2-acetic acid, 5-(3-pyridyl)tetrazole-2-acetic acid, 5-(2-pyrimidyl)tetrazole-2-acetic acid, 5-(2-pyrazinyl)tetrazole-2-acetic acid[8]. Taking all the observations into consideration, in this paper, Hatza (Hatza=5-aminotetrazole-1-acetic acid), Hpytza (Hpytza=5-(4-pyridyl)tetrazole-2-acetic acid), H_2datza (H_2datza=N,N'-di(tetrazol-5-yl)anime-N2,N2'-diacetic acid), H_3tzpha (H_3tzpha=1,3,5-tris(tetrazol-5-yl)benzene-N2,N2',N2''-trisacetic acid) (Scheme1) have been chosen to react with zinc salts, $[Zn(atza)_2(H_2O)_4]$ (**1**), $[Zn(pytza)_2]$ (**2**), $[Zn(datza)(H_2O)_2]\cdot 3H_2O$ (**3**) and $[Zn_3(tzpha)_2(H_2O)_{12}]\cdot MeOH\cdot EtOH\cdot 4H_2O$ (**4**) have been obtained. We anticipate that the four ligands can display more coordination modes and the crystal structures will vary from each other since the structures can be quite unpredictable when the 5-substituted group of the tetrazole ring is replaced by amino group, pyridyl ring or even other tetrazole-carboxylate groups. In this paper, we will describe their synthesis, crystal structures, the influence of the 5-substituted group of the tetrazole ring as well as the luminescence properties of compounds **1** to **4**.

Scheme 1 here

2. Experimental section

2.1 Materials and Apparatus

The ligands were prepared according to the literature methods[9]. Other chemicals were commercially available reagents of analytical grade and used without further purification. The elemental analysis for C, H and N were obtained on a Perkin-Elmer 2400 microanalyzer. The IR spectra were recorded (4000-400 cm^{-1}) on a NICOLET 380 spectrometer with pressed KBr pellets. The photoluminescence spectra were recorded on a Hitachi F4600 spectrofluorometer. The luminescence properties of compounds **1** to **4** were investigated at room temperature in the solid state.

2.2 Synthesis of [Zn(atza)$_2$(H$_2$O)$_4$] (**1**)

Hatza (0.0572g, 0.4mmol) was dissolved in 4mL distilled water and the pH value was adjusted to 6 with KOH (0.2M), then $ZnSO_4\cdot7H_2O$ (0.0576g, 0.2mmol) was added to the solution. The mixture was heated at 80°C with stirring for 2 hours and then cooled to room temperature. Slow evaporation gave rise to the formation of colorless crystals of **1**. For **1**, yield: 35% based on Zn. Anal. Calcd. for $C_6H_{12}N_{10}O_8Zn$: C, 17.26; H, 2.90; N, 33.54%. Found: C, 17.43; H, 2.80; N, 33.76%. IR (KBr, cm^{-1}): 3320(s), 3189(s), 1638(s), 1538(s), 1498(m), 1427(m), 1398(s), 1316(m), 1280(m), 1138(w), 1116(w), 1071(w), 1005(w), 824(m), 761(w), 733(w), 697(m), 617(w).

2.3 Synthesis of [Zn(pytza)$_2$] (**2**)

Hpytza (0.0205g, 0.1mmol) was dissolved in 3.5mL distilled water and the pH value was adjusted to 6 with KOH (0.2M), then a mixture of $ZnSO_4\cdot7H_2O$ (0.1mmol) and ethanol (3mL) was added to the solution, which was sealed in a 25mL telfon stainless steel container and heated at 120°C for 48 h and then cooled to room temperature at a rate of 5 °C/h. Light yellow crystals of **2** were obtained. For **2**, yield: 45% based on Zn. Anal. Calcd. for $C_{16}H_{12}N_{10}O_4Zn$: C, 40.56; H, 2.55; N, 29.57%. Found: C, 40.73; H, 2.50; N, 29.76%. IR (KBr, cm^{-1}): 1668(m), 1624(s), 1590(m), 1565(w), 1455(w), 1425(w), 1385(s), 1265(w), 1050(w), 727(m), 683(m).

2.4 Synthesis of [Zn(datza)(H$_2$O)$_2$]·3H$_2$O (**3**)

H_2datza (0.0538 g, 0.2 mmol) was dissolved in MeOH (5 mL) and water (2 mL), and the pH value was adjusted to 6 with KOH (0.2M), then $ZnCl_2·4H_2O$ (0.021g, 0.1 mmol) was added. The mixture was stirred at 120°C for 48 h and then cooled to room temperature at a rate of 5 °C/h, colorless block crystals of **3** were obtained. For **3**, yield: 51% based on Zn. Anal. Calcd. for $C_6H_{15}N_9O_9Zn$: C, 17.05; H, 3.58; N, 29.83%. Found: C, 17.10; H, 3.50; N, 29.76%. IR (KBr, cm^{-1}): 3412 (s), 1643 (s), 1568 (s), 1451 (m), 1396 (s), 1100 (m), 849 (m), 676 (m).

2.5 Synthesis of $[Zn_3(tzpha)_2(H_2O)_{12}]·MeOH·EtOH·4H_2O$ (**4**)

H_3tzpha (0.0456g, 0.1mmol) was dissolved in a mixture of 1mL ethanol and 1mL distilled, then the pH value was adjusted to 6 with KOH (0.2M). Then a mixture of 3mL methanol and $Zn(NO_3)_2·6H_2O$ (0.0634g, 0.2mmol) was added to the solution, which was heated at 60°C with stirring. Then the solution was cooled to room temperature and slow evaporation gave rise to the formation of colorless crystals of **4**. For **4**, yield: 40% based on Zn. Anal. Calcd. for $C_{36}H_{70}N_{24}O_{32}Zn_3$: C, 27.94; H, 4.56; N, 21.73%. Found: C, 27.82; H, 4.50; N, 21.79%. IR (KBr, cm^{-1}): 3451(s), 1623(s), 1440(m), 1421(m), 1384(s), 1301(m), 1202(w), 1156(w), 1069(w), 901(w), 839(m), 749(w), 705(m), 681(m).

2.6 X-Ray crystallography

Single crystal X-ray crystal data were collected on a Rigaku SCX mini CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.071073 Å). The intensity data were collected by the ω scan technique and were reduced using the Crystal-Clear program[10], and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined on F^2 by full matrix least squares using SHELXTL[11]. All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they were bonded. Selected bond lengths and angles are listed in Table **1**. Crystallographic data are summarized in Table **S1**. Hydrogen-bonding parameters are given in Table **S2**. Compounds **1-4** are deposited with CCDC number 1047132-1047135.

Table 1 here

3. Results and discussions

3.1 Synthesis consideration and general characterization of compounds **1-4**

Compound **1** can be prepared under either ambient or high temperature. Compound **2**, however, can be only obtained under hydrothermal conditions. No compounds formed when $Zn(NO_3)_2\cdot6H_2O/Zn(ClO_4)_2\cdot6H_2O/ZnCl_2\cdot6H_2O/Zn(OAc)_2\cdot6H_2O$ are substitute for $ZnSO_4\cdot7H_2O$, showing that the temperature and counter anion are crucial to the formation of this compound. Compounds **3** and **4** can be prepared . Compounds **1** to **4** are both air stable. The elemental analysis shows that the components of these complexes are well in accordance with the results of the structural analysis. The peaks at 3189-3451 cm^{-1} for compounds **1**, **3** and **4** can be attributed to the O-H stretching vibration of the free or coordinated water molecules while compound **2** does not show a similar peak in that it contains neither guest water nor coordinated water in the molecule. The characteristic bands of carboxylate groups appeared in the usual region at 1623~1643 cm^{-1}[12]. These are correspondent to the results of the X-ray diffraction analysis.

3.2 Crystal structure of $[Zn(atza)_2(H_2O)_4]$ (**1**)

The X-ray analysis reveals that compound **1** crystallizes in triclinic lattice space group $P\bar{1}$ and the asymmetric unit contains one Zn(II) ion, one atza anion, and two water molecules. As is shown in Fig.1, each Zn(II) center is six-coordinated by four oxygen atoms from four water molecules (O3, O3A, O4,O4A) and two oxygen atoms from two carboxylate groups (O1,O1A), forming a distorted octahedral coordination arrangement. Each atza acts as a monodentate ligand to connect to one Zn(II) center, whereas nitrogen atoms are uncoordinated, thereby giving a mononuclear structure.

The Zn-O distances ranges from 2.074-2.138Å, which are similar to those of other zinc compounds[12]. Adjacent mononuclear units are further held together by various hydrogen bonds to generate a 3D supramolecular network (TableS2, figS1).

Fig1 here

3.3 Crystal structure of [Zn(pytza)$_2$] (**2**)

Compound **2** consists of one Zn(II) ion, two pytza$^-$ anions with monoclinic lattice space group *C2/c*. Each Zn(II) center in a distorted octahedral coordination arrangement is surrounded by four oxygen atoms from two carboxylate groups of two pytza ligands (O1,O1C,O2,O2D) and two nitrogen atoms from two pyridyl ring (N5A, N5B) of two pytza ligands (Fig2). Each pytza ligands acts as a tridentate ligand to coordinate to three independent Zn(II) centers via the nitrogen atom and the carboxylate group in a $\mu_{1,3}$-COO *syn-syn* bridging mode, forming a three dimensional network. To understand the 3D topology, the ligands are viewed as green balls (Fig3). The structure can be further simplified as an 8-connect (3^6,4^{16},5^6) tsi network topology(Fig4). The Zn-O bond lengths ranging from 2.099 to 2.131Å are in well accordance with the previously reported zinc compounds [8c,12], so are the Zn-N distances [13]. Compared to that of [Zn(2-pytza)$_2$(H$_2$O)$_2$] or [Zn(3-pytza)$_2$(H$_2$O)$_2$]·2H$_2$O where 2-pytza=5-(2-pyridyl)tetrazole-2-acetato and 3-pytza=5-(3-pyridyl)tetrazole-2-acetic, the structure of compound **2** is substaintially distinct since 5-(2-pyridyl)tetrazole-acetato usually adopts the classic N,N' chelating mode and 5-(3-pyridyl)tetrazole-2-acetato only acts as a bidentate ligand via the pyridine-C and one of the carboxylate-O atoms. Therefore, compound **2** is a three-dimensional network rather than a mononuclear one or a 1D chain. In contrast with compound **1**, when the amino group is replaced by the pyridine ring which can act as a bridging ligand, the coordination site of pytza increases and the structure transfers from a mononuclear one to a three dimensional one. It is worthwhile to point out that compound **2** contains neither coordinated molecules nor guest solvent ones, which differs from the other three compounds in the article. Non-classic hydrogen bonds exist between the C-H group of the pyridyl group and the oxygen atom of the carboxylate group [C(6)—H(6) ···O(1) 2.48Å/124º, C(7)—H(7) ···O(2) 2.40Å/123º] to stabilize the supramolecular assembly (Table S2).

Fig 2-4 here

3.4 Crystal structure of [Zn(datza)$(H_2O)_2$]·$3H_2O$ (**3**)

Compound **3** consists of one Zn(II) anion, one datza^{2-} ligand, two coordinated water molecules and three uncoordinated water molecules in a crystallographically independent asymmetric unit, with triclinic space group $P\bar{1}$. Each Zn(II) center is in a distorted octahedral coordination arrangement whose coordination sites are occupied by two tetrazole nitrogen atoms (N1B, N9B) and carboxylate oxygen atoms (O2, O5A) and water molecules (O3, O4) (Fig.5). The Zn-N bond distances are 2.144-2.174Å and Zn-O distances fall in the range of 2.053-2.138Å, which are similar to those of reported zinc complexes [13]. Each datza^{2-} acts as a tetradentate ligand via two nitrogen atoms of two tetrazolyl rings with a chelating mode(N1, N9) and two oxygen atoms of the carboxylate group with a bridging mode (O1, O5). Two such ligands set up a double bridge between neighboring Zn(II) ions, forming a 1D extending along the *a* axis with the Zn···Zn distance of 5.945(2) Å. When the amino group is replaced by the tetrazole-carboxylate group, datza adopts a N(tetrazole),N'(tetrazole) chelating mode, and further bridge two Zn(II) centers by the carboxylate to form a ladder-like chain. Adjacent 1D chains are further connected by O-H···O hydrogen bonds and C-H···N hydrogen bond and N-H···O hydrogen bond to generate a 3D network (TableS2,FigS2). The 3D net topology contains rhomboidal grids with the diagonal lengths of the rhomboidal grids being 13.5346(37) Å.

Fig 5 here

3.5 Crystal structure of $[Zn_3(tzpha)_2(H_2O)_{12}]\cdot MeOH\cdot EtOH\cdot 4H_2O$ (**4**)

The X-ray analysis reveals that compound **4** crystallizes in triclinic lattice space group $P\bar{1}$. As shown in Fig.6, each Zn(II) ion is six-coordinated by two oxygen atoms of the carboxylate group from two independent tzpha^{3-} ligands and four oxygen atoms from four water molecules. The Zn-O distances ranges from 2.068 to 2.120 Å [13], so the coordination arrangement can be described as a slightly distorted octahedron. Each tzpha^{3-} acts as a tridentate ligand to connect to three Zn(II) centers via two carboxylate-O atoms in a $\mu_{1,3}$-COO *syn-syn* bridging or a monodentate mode, whereas the third carboxylate group is uncoordinated, therefore, compound **4** displays a one dimensional chain extending along the *c* axis (Fig7a). When the amino group is replaced by the bitetrazole-carboxylate benzene, only the carboxylate-O atoms are coordinated to the Zn(II) center, whereas the tetrazole rings are uncoordinated. The structure can be simplified as a beaded chain and the diagonal lengths of the rhomboidal grids are 15.6425 and 15.685Å, respectively (Fig.7b). Adjacent 1D chains are further held together by various hydrogen bonds to generate a three dimensional supramolecular network (TableS2, FigS3).

Fig6-7 here

3.6 Discussion of coordination modes and structures

In this work, we have selected four new tetrazole-carboxylate ligands to react with zinc salts in order to investigate the influence of the different 5-substituted group of the tetrazole ring on the crystal structures of resulting complexes. Four new coordination compounds based on Hatza, Hpytza, H_2datza, H_3tzpha have been successfully constructed. For compound **1**, atza only acts as a monodentate ligand via one of the carboxylate oxygen atoms, the structure is a simple zero dimensional mononuclear one. However, the amino group can form various strong O-H···O, N-H···O hydrogen bonds to stabilize the supramolecular assembly. When the amino group is substituted by the pyridine ring, the coordination sites increases in that both the pyridine-N and carboxylate-O atoms participate in the coordination, therefore, the structure changes to an 8-connect (3^6,4^{16},5^6) tsi network topology while the number of hydrogen bonds decreases sharply simultaneously. When the number of the tetrazolyl rings and the carboxylate groups increases from one to two, another coordination mode of datza has been found in compound **3**, where datza^{2-} not only adopts a classic N(tetrazole),N'(tetrazole) chelating mode, but also acts as a bridging ligand and the number of coordination sites adds up to 4. Compound **3**, however, becomes a one dimensional ladder-like chain since only one oxygen atom of the carboxylate group is coordinated to the Zn(II) center, the others being uncoordinated. Theoretically speaking, H_3tzpha with three tetrazole rings and carboxylate groups, should have the most coordination sites, but it adopts a relatively simple coordination mode. This may be explained by stereo effect. Therefore, compound **4** displays a 1D beaded chain which is different from that of compound **3** (a 1D ladder-like chain).

Scheme 2 here

4. Luminescence properties

Inorganic-organic hybrid coordination polymers, especially those based on d^{10} metal centers, have been investigated for fluorescence properties and potential applications as fluorescence-emitting materials [14]. The luminescence of compounds **1-4** and the free ligands were investigated at room temperature in the solid state. 5-aminotetrazole-1-acetic acid, 5-(4-pyridyl)tetrazole-2-acetato potassium salt, N,N-di(tetrazol-5-yl)amine-N2,N2'-diacetate,1,3,5-tris(tetrazol-5-yl)benzene-N2,N2', N2''-trisacetic acid exhibit photoluminescence with maximum intensity at 445, 429, 401 and 422 nm upon excitation at 308, 370, 307 and 372 nm, respectively. Compounds **1-4** show maximum emission at 469, 442, 423 and 417 nm upon excitation at 360, 370, 313 and 380 nm, respectively (Fig8). Compared to the corresponding ligands, a red shift of 24 nm for **1**, 13 nm for **2**, 22 nm for **3**, and a blue shift of 5 nm for **4** have been observed, respectively, which are in well accordance with those of the previously reported zinc complexes [12]. Therefore, these emissions can be ascribed to ligand centered luminescence. Generally, the intraligand fluorescence emission wavelength is determined by the energy gap between the π and π* molecular orbitals of the free ligand, which is related to the extent of π conjugation[12]. Compounds **1-4** show even stronger emission because the coordination of Zn(II) further enlarges the conjugated system to enhance the luminescence.

Fig 8 here

5. Conclusions

In summary, we are the first to report the four novel zinc coordination compounds based on Hatza, Hpytza, H_2datza and H_3tzpha. The structures are controlled by not only the number and different coordination modes of the tetrazole-carboxylate but also the complementary hydrogen bonds. These compounds show outstanding luminescence properties, compared to the ligand. Our research results indicates that as promising ligands, Hatza, Hpytza, H_2datza and H_3tzpha have great potentials in the field of coordination compounds and further explorations are underway in our work group.

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Scheme **1** Schematic drawing for Hatza, Hpytza, H_2datza and H_3tzpha
Scheme **2** The influence of different substituted group of the tetrazole ring on the structure of compounds **1**-**4**.
Table **1** Selected bond distances (Å) and angles (º) for **1-4**
Fig.**1** The mononuclear structure in compound **1**, showing coordination environment of Zn(II).
Fig.**2** The coordination environment of Zn(II) in compound **2**. Hydrogen atoms are omitted for clarity
Fig.**3** The 3D network structure of compound **2**, pytza ligands are simplified as green balls. (a) view along the *b* axis; (b) view along the *c* axis; Hydrogen atoms are omitted for clarity
Fig.**4** The 3D 8-connect (3^6,4^{16},5^6) tsi network of compound **2**.
Fig.**5** The coordination environment of Zn(II) in compound **3**. Hydrogen atoms are

omitted for clarity.

Fig.**6** The coordination environment of Zn(II) in compound **4**. Hydrogen atoms are omitted for clarity.

Fig.**7** The 1D chain structure of compound **4** extending along the *c* axis. Hydrogen atoms are omitted for clarity.

Fig.**8** The emission spectra of Hatza, Hpytza, H_2datza, H_3tzpha and compounds **1** to **4** at room temperature in the solid state.

Table **S1** Selected crystallographic data and structure refinement for compounds **1-4.**

Table **S2** Hydrogen-bonding Geometry (Å and º) for compounds **1-4**

Fig.**S1** The 3D network structure of **1** formed via hydrogen bonding interactions.

Fig.**S2** The 3D network structure of compound **3** formed via hydrogen bonding interactions.

Fig.**S3** The 3D network structure of **4** formed via hydrogen bonding interactions.

Fig **S4** The excitation spectra of compounds **1** to **4**.

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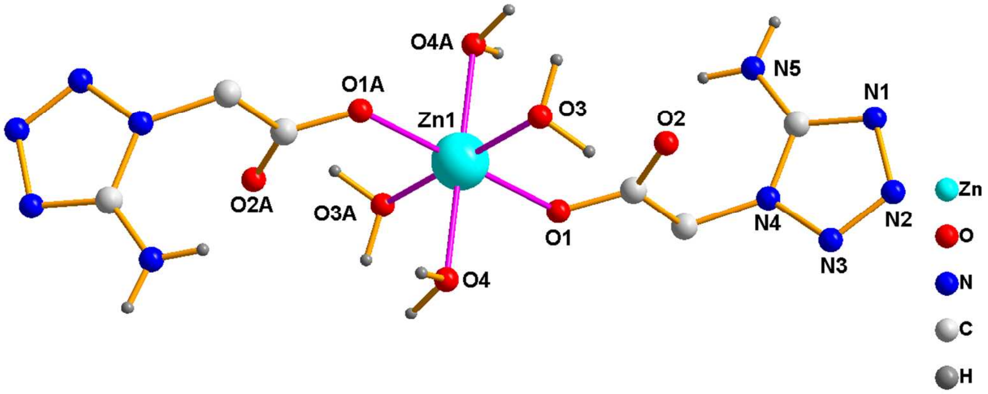
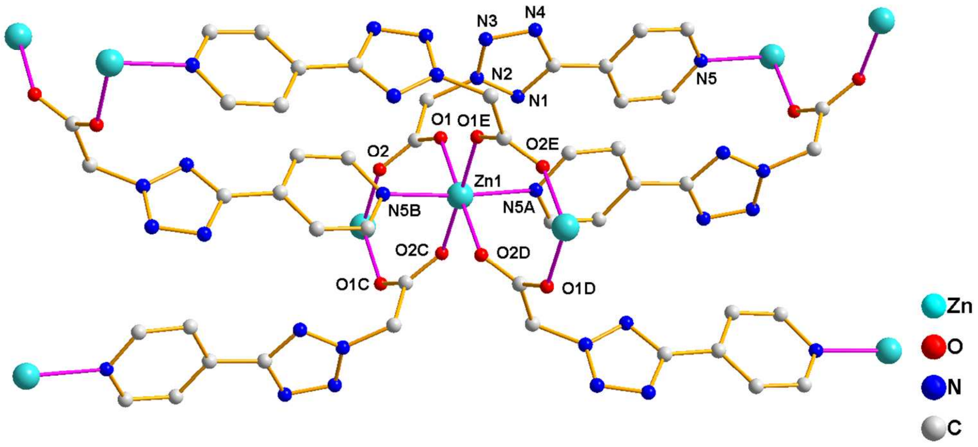


352x176mm (96 x 96 DPI)



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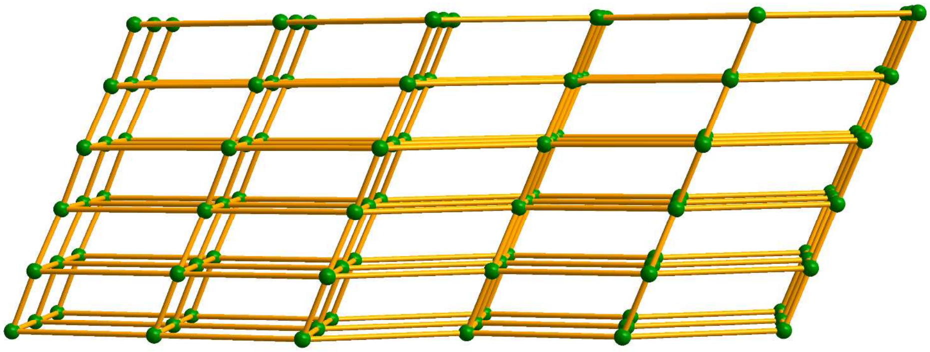

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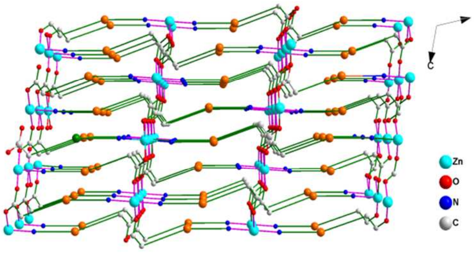
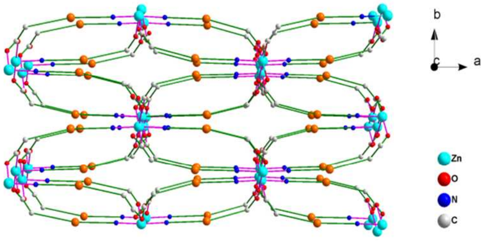

a
c
Zn
O
N
C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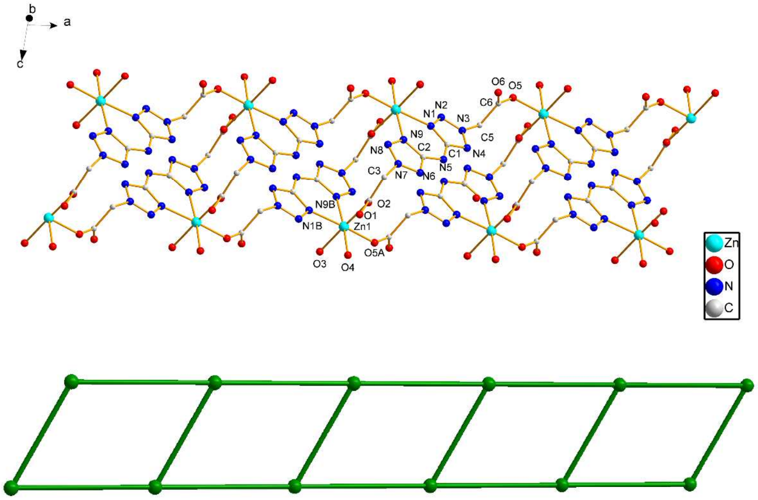
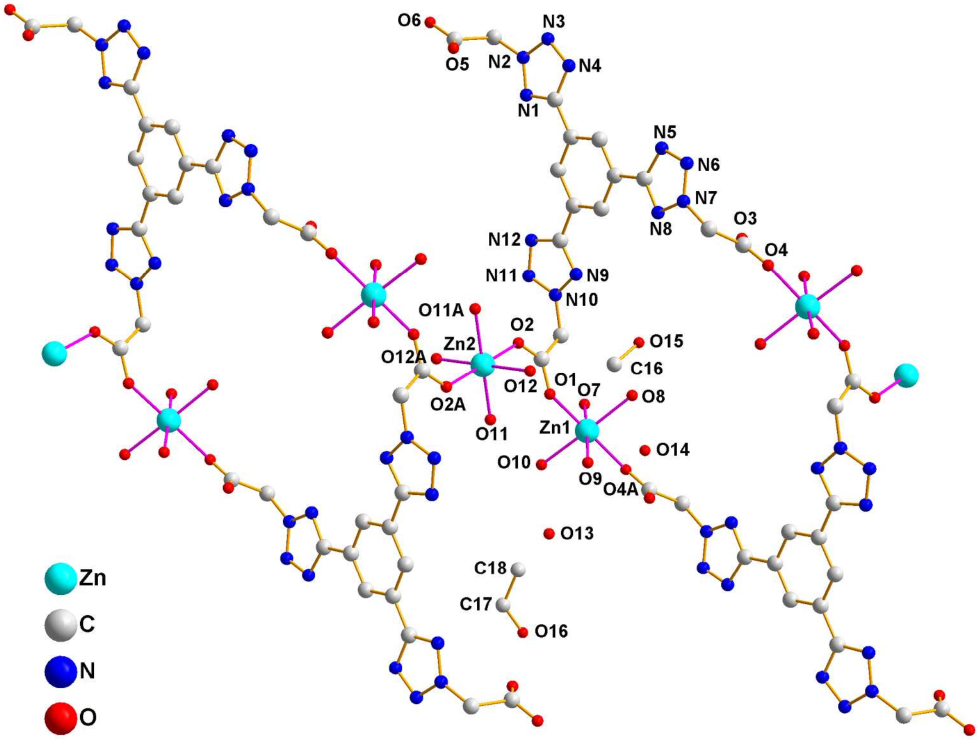
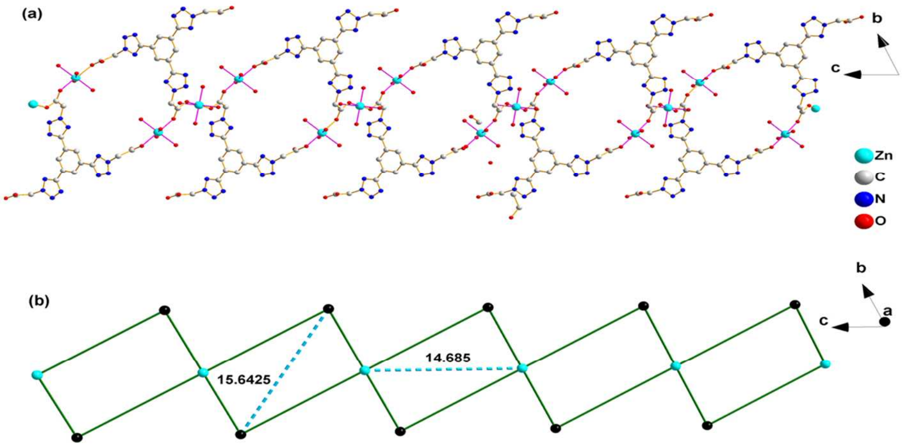


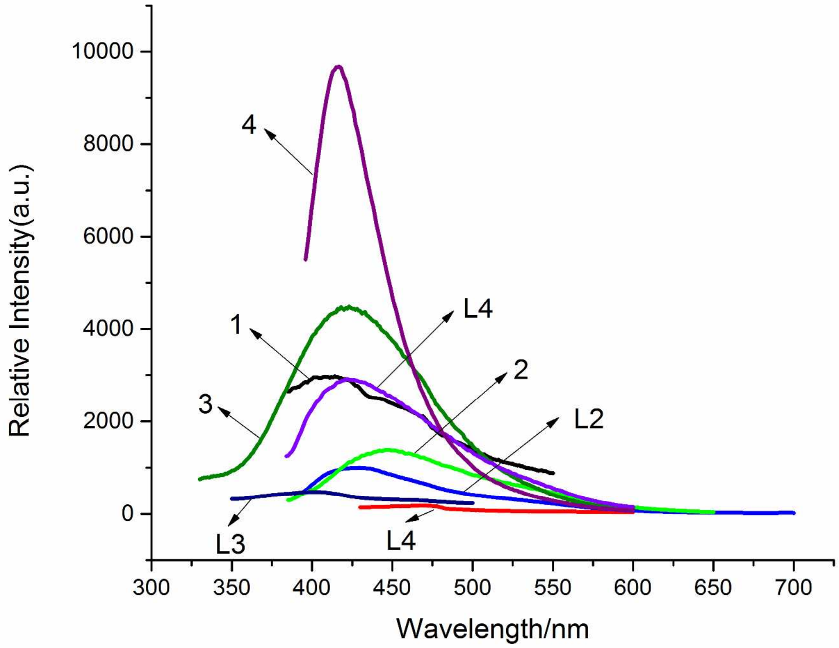
1719x1058mm (96 x 96 DPI)



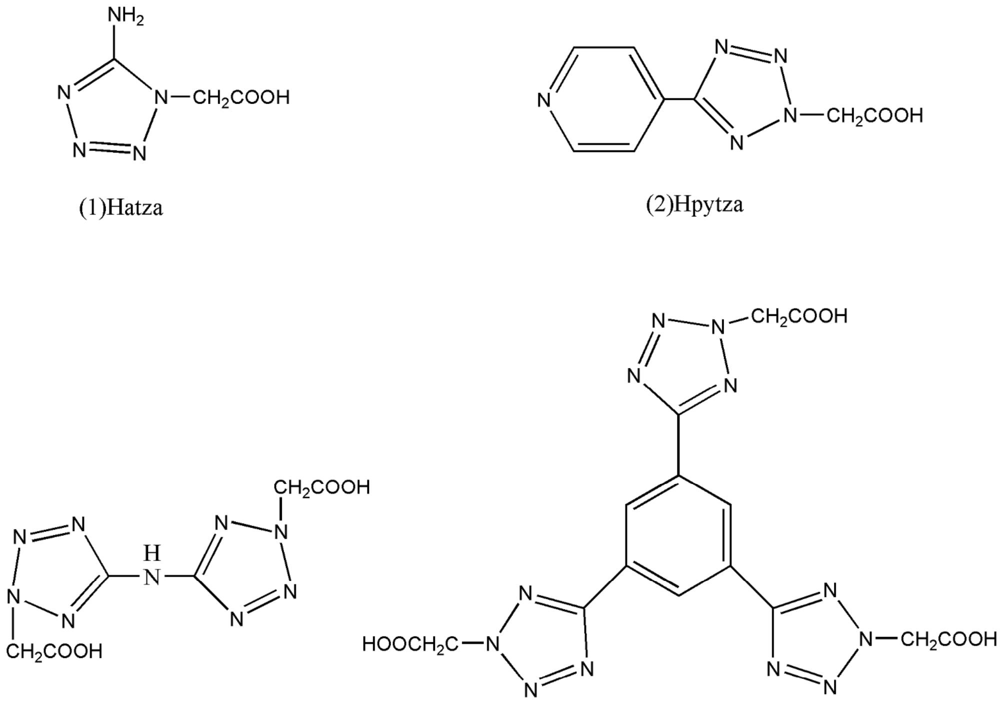
608x484mm (96 x 96 DPI)



358x168mm (95 x 95 DPI)



279x215mm (300 x 300 DPI)



(1)Hatza

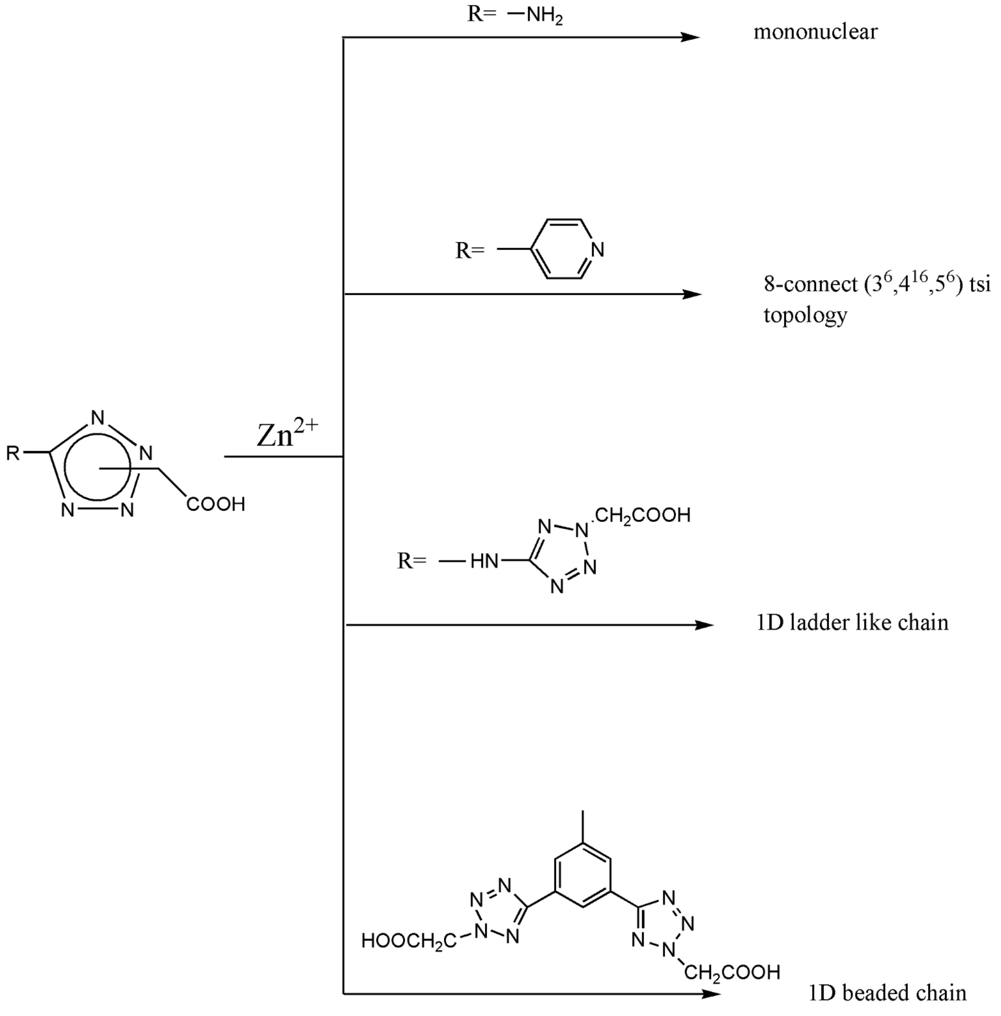
(2)Hpytza

(3)H_2datza

(4)H_3tzpha

Scheme

176x152mm (300 x 300 DPI)



177x179mm (300 x 300 DPI)

Table**1**. Selected bond distances (Å) and angles (º) for **1-4**

[Zn(atza)$_2$(H$_2$O)$_4$](**1**)

Zn(1)–O(1A)	2.074(2)	Zn (1)–O(1)	2.074(2)
Zn (1)–O(4)	2.128(2)	Zn(1)–O(4A)	2.128(2)
Zn(1)–O(3A)	2.138(2)	Zn (1)–O(3)	2.138(2)
O(1A)–Zn (1)–O(1A)	180.00(13)	O(1A)–Zn (1)–O(4)	92.70(10)
O(1)–Zn (1)–O(4)	87.30(10)	O(1A)–Zn (1)–O(4A)	87.30(10)
O(1)–Zn (1)–O(4A)	92.70(10)	O(4)–Zn (1)–O(4A)	180.0
O(1A)–Zn (1)–O(3A)	92.67(10)	O(1)–Zn (1)–O(3A)	87.33(10)
O(4)–Zn (1)–O(3A)	88.02(10)	O(4A)–Zn (1)–O(3A)	91.98(10)
O(1A)–Zn (1)–O(3)	87.33(10)	O(1)–Zn (1)–O(3)	92.67(10)
O(4)–Zn (1)–O(3)	91.98(10)	O(4A)–Zn (1)–O(3)	88.02(10)
O(3A)–Zn (1)–O(3)	180.000(1)		

[Zn(pytza)$_2$](**2**)

Zn(1)–O(1)	2.099(3)	Zn (1)–O(2B)	2.131(3)
Zn(1)–N(5A)	2.177(3)		
O(1E)–Zn (1)–O(1)	88.31(15)	O(1E)–Zn (1)–O(2D)	178.82(11)
O(1)–Zn (1)–O(2D)	90.69(15)	O(1)–Zn (1)–O(2C)	90.32(15)
O(1E)–Zn (1)–N(5A)	92.75(11)	O(1)–Zn (1)–N(5B)	83.81(11)
O(2D)–Zn (1)–N(5A)	83.81(11)	O(2C)–Zn (1)–N(5A)	87.77(11)
O(2C)–Zn (1)–N(5A)	95.61(11)	O(1E)–Zn (1)–N(5A)	180.00(9)
N(5A)–Zn (1)–N(5B)	175.22(11)		

[Zn(datza)(H$_2$O)$_2$]·3H$_2$O (**3**)

Zn(1)–O(2)	2.052 (3)	Zn(1)–O(4)	2.080(3)
Zn(1)–O(5A)	2.089 (5)	Zn(1)–O(3)	2.138(3)
Zn(1)–N(9B)	2.145 (6)	Zn(1)–N(1B)	2.177 (5)
O(2)–Zn(1)–O(4)	91.61 (12)	O(2)–Zn(1)–O(5A)	91.58 (17)

O(4)–Zn(1)–O(5A)	89.39 (16)	O(2)–Zn(1)–O(3)	177.15(16)
O(4)–Zn(1)–O(3)	89.55 (11)	O(5A)–Zn(1)–O(3)	85.83 (17)
O(2)–Zn(1)–N(9B)	90.07 (18)	O(4)–Zn(1)–N(9B)	174.86(18)
O(5A)–Zn(1)–N(9B)	95.4 (2)	O(3)–Zn(1)–N(9B)	88.99(18)
O(2)–Zn(1)–N(1B)	94.73 (17)	O(4)–Zn(1)–N(1B)	94.83 (16)
O(5A)–Zn(1)–N(1B)	172.3 (2)	O(3)–Zn(1)–N(1B)	87.76 (17)
N(9B)–Zn(1)–N(1B)	80.2 (2)		

$[Zn_3(tzpha)_2(H_2O)_{12}]\cdot MeOH\cdot EtOH\cdot 4H_2O$ (**4**)

Zn (1)–O(8)	2.068(8)	Zn (1)–O(7)	2.071(8)
Zn (1)–O(1)	2.085(6)	Zn (1)–O(10)	2.108(7)
Zn (1)–O(9)	2.117(7)	Zn (1)–O(4A)	2.120(6)
Zn (2)–O(11A)	2.080(6)	Zn (2)–O(11)	2.080(6)
Zn (2)–O(12)	2.079(7)	Zn (2)–O(12A)	2.079(7)
Zn (2)–O(2)	2.097(6)	Zn (2)–O(2A)	2.097(6)
O(8)–Zn(1)–O(7)	87.9(4)	O(8)–Zn(1)–O(1)	89.7(3)
O(7)–Zn(1)–O(1)	96.4(3)	O(8)–Zn(1)–O(10)	175.5(3)
O(7)–Zn(1)–O(10)	87.6(3)	O(1)–Zn(1)–O(10)	91.1(3)
O(8)–Zn(1)–O(9)	96.2(3)	O(7)–Zn(1)–O(9)	175.6(3)
O(1)–Zn(1)–O(9)	85.5(3)	O(1O)–Zn(1)–N(9)	88.4(3)
O(8)–Zn(1)–O(4A)	89.3(3	O(7)–Zn(1)–O(4A)	88.7(3)
O(1)–Zn(1)–O(4A)	174.8(3)	O(10)–Zn(1)–O(4A)	90.4(3)
O(9)–Zn(1)–O(4A)	89.5(3)	O(11A)–Zn(2)–O(11)	180.0(2)
O(11A)–Zn(2)–O(12)	87.7(3)	O(11)–Zn(2)–O(12)	92.3(3)
O(11A)–Zn(2)–O(12A)	92.3(3)	O(11)–Zn(2)–O(12A)	87.7(3)
O(12A)–Zn(2)–O(12A)	180.000(1)	O(11A)–Zn(2)–O(2)	90.6(2)
O(11)–Zn(2)–O(2)	89.4(2)	O(12)–Zn(2)–O(2)	91.5(3)
O(12A)–Zn(2)–O(2)	88.5(3)	O(11A)–Zn(2)–O(2A)	89.4(2)
O(11)–Zn(2)–O(2A)	90.6(2)	O(12)–Zn(2)–O(2A)	88.5(3)

O(12)–Zn(2)–O(2A)	91.5(3)	O(2)–Zn(2)–O(2A)	180.000(1)

Symmetry code

For **1**: A: -x, 2-y, 1-z.

For **2**: A: 0.5-x, 0.5-y, -z;B: -0.5+x,0.5-y, -0.5+z; C: -x, 1-y, z; D: x, 1-y, -0.5+z; E: -x, y, -0.5-z

For **3**: A: -*x*+1, -*y*, -*z*; B: -*x*, -*y*, -*z*

For **4**: A: -x, 2-y, -z.