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Structure modulation in zinc–ditetrazolate coordination polymers by *in situ* ligand synthesis†

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Three new Zn^{II}–ditetrazolate coordination polymers (CPs), namely [Zn(*m*-pdtz)(4,4'-bipy)(H₂O)]_n (**1**), [Zn₂Cl₂(*m*-pdtz)(4,4'-bipy)]_n (**2**) and [Zn₂(OH)₂(*m*-pdtz)]_n (**3**) (4,4'-bipy = 4,4'-bipyridine, *m*-H₂pdtz = 5,5'-1,3-phenylene-ditetrazole), have been constructed by an *in situ* ditetrazolate-ligand synthesis system. The formation of *m*-pdtz²⁻ ligand involves the Sharpless [2 + 3] cycloaddition reaction between isophthalonitrile (IPN) and NaN₃ in the presence of Zn²⁺ ions as Lewis-acid catalysts under hydro/solvothermal conditions. Single-crystal structural analyses reveal that compound **1** exhibits a new 6-connected 3D structural topology constructed from dimeric {Zn₂} clusters as secondary building units (SBUs), compound **2** represents a 2D sql structural feature built from rhombic tetrameric {Zn₄} rings as SBUs, while compound **3** displays a new (4,6)-connected 3D structural topology constructed from rod-shaped 1D Zn-chains as SBUs. Regarding these three CPs, we have performed a thorough investigation on their crystal structure, topology, and fluorescence property.

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Introduction

The design and synthesis of coordination polymers (CPs) have stimulated the interest of chemists in recent years because of their charming architectures and potential applications in a variety of scientific fields like nanoscale magnetism,¹ catalysis,² gas storage and separation,³ drug delivery,⁴ and sensor devices.⁵ From a synthetic point of view, the judicious selection of appropriate organic ligands are proved to be one of the most critical factors to manipulate the versatile structures of CPs.^{6–10} Among multitudinous organic ligands, ditetrazolates-containing ligands, in particular, have proved to be good candidates for the construction of novel CPs due to their multidentate nature, which endows them flexible and diverse coordination modes.¹¹ Specifically, the ditetrazolates with two tetra-N-donor can provide more coordination sites for metal centers to form complicated frameworks; however, the reports on this class of ligands to prepare new CPs have been far less explored.

Until now, current research mainly involves using two effective strategies to construct the CPs based on tetrazolate-

containing ligands.^{11–15} The first and the most common strategy is ligand availability, which directly introduces tetrazolate-containing ligands into synthetic system, such as hydrothermal reactions or other conventional synthesis.^{11a–d,12,13} The use of available tetrazolate-containing ligands would consequently increase the possibility of coordination between organic ligands and metal ions, thus benefiting us to obtain splendid structures in target CPs. The appropriate tetrazolate-containing ligands can be artificially designed, synthesized and modified by the mature technique of organic synthesis. So this strategy has found wide applications and has been applied successfully in many examples of CPs.^{11a–d,12,13}

The second strategy of achieving tetrazolate-based CPs is to construct the CPs from the famous *in situ* ligand synthesis system of Sharpless [2 + 3] cycloaddition reactions between cyano precursors and azide groups in a hydrothermal environment with various transition metal ions as the Lewis acid catalysts.^{11e–h,14,15} As references demonstrated, this method also suggests a preeminent route for the exploration of novel tetrazolate-based CPs. In contrast to the first strategy, this system can fabricate more fascinating structures because it has more potential factors to create, modulate or influence the structural diversities during the assembly process. Recently, this approach has also been successfully implemented to construct some wonderful CPs exhibiting interesting properties.^{11e–h,14,15}

In addition, a careful selection of the different synthetic condition, such as metal–ligand ratio, solvent, and auxiliary ligand, is a key step for the effective design of CPs with specific structural modulation. In this paper, we want to adjust the metal

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coordination modes by changing the metal–ligand ratio in order to influence the dimensionality of the CPs. At the same time, we can change the solvent system to achieve the different nuclear degree of the metal. More important, we also introduce the auxiliary ligand, such as the rigid long chain-like N-donor 4,4'-bipy, to induce the potential structural transformations, mainly because of its propensity to form voids or frameworks structures.

In view of this, we draw lessons from the latter strategy and exploited *in situ* ditetrazolate-ligand synthesis of IPN, NaN_3 and ZnCl_2 , which consequently led to the formation of three new CPs $[\text{Zn}(m\text{-pdtz})(4,4'\text{-bipy})(\text{H}_2\text{O})]_n$ (**1**), $[\text{Zn}_2\text{Cl}_2(m\text{-pdtz})(4,4'\text{-bipy})]_n$ (**2**) and $[\text{Zn}_2(\text{OH})_2(m\text{-pdtz})]_n$ (**3**). Herein, the formation of $m\text{-pdtz}^{2-}$ ligand involves the *in situ* Sharpless [2 + 3] cycloaddition reaction between IPN and NaN_3 in the presence of Zn^{2+} ion as a Lewis-acid catalyst under hydro/solvothermal conditions.¹⁶ Among the resulting CPs, compound **1** exhibits a new 6-connected 3D structural topology constructed from dimeric $\{\text{Zn}_2\}$ clusters as SBUs (secondary building units), and compound **2** represents a 2D **sql** structural feature built from rhombic tetrameric $\{\text{Zn}_4\}$ rings as SBUs, while compound **3** displays a new (4,6)-connected 3D structural topology constructed from rod-shaped 1D Zn-chains as SBUs. In this work, both the crystal structures and topological analyses of CPs **1–3** have been investigated in detail, as well as the exploration of their fluorescence properties.

Experimental

Materials and methods

All chemicals were commercially purchased and used as received.

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectra were carried out by the single-crystal data and diffraction-crystal module of the mercury (Hg) program available. IR spectrum was measured in the range of 400–4000 cm^{-1} on a Tensor 27 OPUS FT-IR spectrometer using KBr pellets (Bruker, German). Fluorescence spectra were recorded at room temperature on a Varian Cary Eclipse fluorescence spectrometer (Varian, USA). Fluorescence lifetime were measured on an Edinburgh Instruments FLS920P equipped with a Xe lamp-900 and μF920 as the excitation light source. Solid state UV-vis spectra were recorded at room temperature on a Varian Cary 5000 Spectrophotometer in the wavelength range of 200–800 nm.

Synthesis of CPs 1–3

$[\text{Zn}(m\text{-pdtz})(4,4'\text{-bipy})(\text{H}_2\text{O})]_n$ (**1**). A mixture of ZnCl_2 (68 mg, 0.5 mmol), IPN (38 mg, 0.3 mmol), NaN_3 (65 mg, 1 mmol), 4,4'-bipy (47 mg, 0.3 mmol) and H_2O (8 mL) were sealed in a 23 mL Teflon lined stainless steel container, which was heated at 160 °C for 3 days and then cooled to room temperature at a rate of 10 °C h^{-1} . Colourless block shaped crystals of **1** were collected. Yield: 20% for **1** based on Zn. Elemental analysis (%) for **1**, $\text{C}_{18}\text{H}_{14}\text{N}_{10}\text{OZn}$ ($M = 451.78$): calcd: 47.85; H, 3.12; N, 31.00; found: C, 47.92; H, 3.08; N, 31.04.

$[\text{Zn}_2\text{Cl}_2(m\text{-pdtz})(4,4'\text{-bipy})]_n$ (**2**). A mixture of ZnCl_2 (136 mg, 1 mmol), IPN (38 mg, 0.3 mmol), NaN_3 (65 mg, 1 mmol), 4,4'-bipy (47 mg, 0.3 mmol) and H_2O (8 mL) were sealed in a 23 mL Teflon

Table 1 Crystal data and structure refinements for **1–3**

	1	2	3
Formula	$\text{C}_{18}\text{H}_{14}\text{N}_{10}\text{OZn}$	$\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{N}_{10}\text{Zn}_2$	$\text{C}_8\text{H}_6\text{N}_8\text{O}_2\text{Zn}_2$
CCDC no.	1407193	1407194	1407194
Size (mm)	$0.20 \times 0.18 \times 0.18$	$0.22 \times 0.17 \times 0.16$	$0.22 \times 0.18 \times 0.16$
Formula weight	451.78	570.08	377.00
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$
a (Å)	20.622(8)	9.0585(18)	8.1044(16)
b (Å)	9.858(2)	11.245(2)	16.023(3)
c (Å)	19.482(4)	11.283(2)	10.137(4)
α (°)	90	94.55(3)	90
β (°)	117.55(3)	108.18(3)	117.31(2)
γ (°)	90	93.49(3)	90
V (Å ³)	3511.4(17)	1084.0(3)	1169.6(6)
Z	8	2	4
D_c (mg m^{-3})	1.709	1.764	2.141
μ (mm ^{−1})	1.436	2.488	4.117
$F(000)$	1839	568	744
Collected reflections	14 819	9492	9859
Unique reflections	3092	3816	2055
R_{int}	0.0637	0.0418	0.0706
R_1^a [$I > 2\sigma(I)$]	0.0533	0.0395	0.0550
wR_2^b [all data]	0.0997	0.0825	0.1103
GOF on F^2	1.138	1.071	1.167
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ^{−3})	0.83, −0.50	0.62, −0.42	0.90, −0.47

$$^a R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|. \quad ^b wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / (\sum w|F_o|^2)^{1/2}].$$

lined stainless steel container, which was heated at 160 °C for 3 days and then cooled to room temperature at a rate of 10 °C h⁻¹. Colourless block shaped crystals of **2** were collected. Yield: 21% for **2** based on Zn. Elemental analysis (%) for **2**, C₁₈H₁₂N₁₀Cl₂·Zn₂ (*M* = 570.08): calcd: C, 49.64; H, 4.57; N, 11.58; found: C, 49.67; H, 4.48; N, 11.63.

[Zn₂(OH)₂(*m*-pdtz)]_n (**3**). A mixture of ZnCl₂ (68 mg, 0.5 mmol), IPN (38 mg, 0.3 mmol), NaN₃ (65 mg, 1 mmol), 1-*H*-tetrazole (21 mg, 0.3 mmol) and H₂O/EtOH (8 mL, *v* : *v* = 1 : 1) were sealed in a 23 mL Teflon lined stainless steel container, which was heated at 160 °C for 3 days and then cooled to room temperature at a rate of 10 °C h⁻¹. Colourless block shaped crystals of **3** were collected. Yield: 22% for **3** based on Zn. Elemental analysis (%) for **3**, C₈H₆N₈O₂Zn₂ (*M* = 377.00): calcd: C, 25.49; H, 1.60; N, 29.72; found: C, 25.56; H, 1.53; N, 29.75.

X-ray crystallography. The crystallographic data of **1**, **2** and **3** were collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo-K α radiation (λ = 0.71073 Å). The crystal data were solved by direct methods and refined by a full-matrix least-square method on *F*² using the SHELXL-97 crystallographic software package.¹⁷ Zinc atoms in **1**, **2** and **3** were found from *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on *F*². The hydrogen atoms of organic ligands, OH⁻ group and lattice water were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. Further details of crystal data and structure refinement for **1**, **2** and **3** were summarized as follows in Table 1. Selected bond lengths and angles of **1**, **2** and **3** were given in Tables S2–S4.† Full crystallographic data for **1**, **2** and **3** have been deposited with the CCDC (1407193 for **1**, 1407194 for **2** and 1407195 for **3**).†¹⁸

Results and discussion

Structures modulation and comparison

In the synthesis process, as introduction mentioned, we carefully select three different synthetic conditions to modulate the structures: the different metal–ligand ratio, different solvents and auxiliary ligand. In compounds **1** and **2**, the synthetic conditions are similar but only the metal–ligand ratio is different. From compound **1** to **2**, the amount of Zn²⁺ ions increases one times, the metal–ligand ratio relative decrease, which reduce the coordination chance for ligand to metal and led to the change of metal coordination modes: the coordination numbers of Zn²⁺ ions reduce from 6 to 4. As a result, the dimensionalities of the CPs reduce from 3D for compound **1** to 2D for compound **2**. Compared compounds **1**, **2** with **3**, there are two different synthetic conditions to influence the structures. Firstly, it is interesting to note that the organic solvents with different sizes, boiling points and polarities play important roles in inducing different structural aggregates of the three compounds, which not only dramatically influence the different dimensionalities of the compounds, but also allow access to new structures and topologies through inducing the different coordination environments of Zn²⁺ ions and linking modes of

m-pdtz²⁻ ligand. Due mainly to the employment of EtOH solvent with bigger steric hindrance, smaller boiling points and polarities than those in H₂O under similar synthetic conditions, distinct framework structures were obtained. By the introducing EtOH in the synthesis system of **3**, the vapor pressure in the Teflon lined stainless steel container is increase, which can improve the solubility and reaction rate of the reactants. As a result, the nuclear degree of the Zn²⁺ ions is increase for forming a binuclear {Zn₂} cluster as SBU and further give a 1D rod-shaped Zn chain. Secondly, we introduce the auxiliary ligand in the compounds **1** and **2**, namely the rigid long chain-like N-donor 4,4'-bipy, to induce the potential structural transformations, mainly because of its propensity to form voids or frameworks structures as the compounds **1** and **2** displayed. While compound **3** is a 3D compact structure by the introduction of smaller OH⁻ group by accident and without the rigid linear 4,4'-bipy sustaining the framework. The result shows that the choice of different metal–ligand ratio, different solvents and auxiliary ligand is clearly critical in determining the molecular architectures of the CPs and has a significant effect on the final structures.

Structural analysis

Structure of [Zn(*m*-pdtz)(4,4'-bipy)(H₂O)]_n (1**).** Single-crystal structural analysis reveals that **1** crystallizes in the monoclinic space group *C2/c* and has a 6-connected 3D structural topology constructed from dimeric {Zn₂} clusters as SBUs. The basic structural unit of **1** contains one Zn²⁺ ion, one *m*-pdtz²⁻ ligand, one 4,4'-bipy ligand and one coordinated H₂O molecule. The asymmetric unit and coordination mode of Zn²⁺ center is shown in Fig. 1a. The Zn²⁺ ion is coordinated with three μ_1 -2 coordinated nitrogen atoms originating from three independent

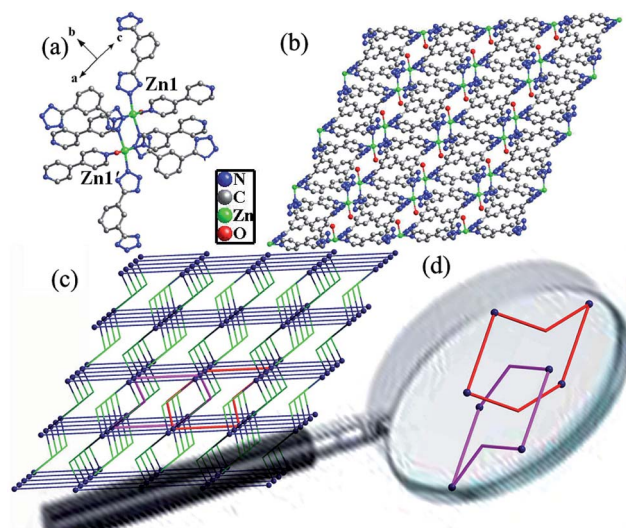


Fig. 1 (a) The ball-and-stick view of the coordination environment of Zn²⁺ in {Zn₂} cluster; (b) the 3D framework in **1**; (c) the schematic view of the 6-connected topology with the *m*-pdtz²⁻ ligands as 2-connected nodes for **1**; (d) the partial enlarged drawing in order to show the *m*-pdtz²⁻ ligands uncrossed feature. Codes: blue, N; gray, C; green, Zn; red, O (the hydrogen atoms have been omitted for clarity).

m -pdtz²⁻ ligands, two nitrogen atoms deriving from two different 4,4'-bipy ligands, and one terminal H₂O molecule to form a hexa-coordinated distorted octahedral geometry. The bond lengths and angles are shown in Table S1.† All m -pdtz²⁻ ligands possess the same tridentate coordination mode (μ_1 -2,2' and μ_2 -2), that is, two adjacent N-donors from one tetrazolate groups (μ_1 -2,2') coordinate with two different Zn²⁺ ions to generate a dimeric {Zn₂} cluster and the third N-donor from the other tetrazolate group (μ_1 -2) coordinates with the third Zn²⁺ ion from another dimeric {Zn₂} cluster. The 4,4'-bipy act only as a bridging ligand to connect two different Zn²⁺ ions from two distinct dimeric {Zn₂} clusters. Based on above coordination modes, all the dimeric {Zn₂} clusters as SBUs are linked by the m -pdtz²⁻ and 4,4'-bipy ligands to form a 3D framework (see Fig. 1b).

From the topological point of view, the dimeric {Zn₂} clusters can be simplified as 6-connected nodes that further links the other six dimeric {Zn₂} clusters *via* four m -pdtz²⁻ ligands and four 4,4'-bipy ligands. Since the 4,4'-bipy ligands involved here act only as linear connection, it is thus not necessary to consider them in the topological analysis. Based on this simplification, the overall 3D network of **1** can be rationalized as a new uninodal 6-connected topology with the Schläfli symbol of {4⁴·6¹¹} (TD10 = 3595) (see Fig. 1c). In order to better understand the topology, we rationalized the m -pdtz²⁻ ligands as 2-connected nodes which can be clearly seen from their uncrossed feature (see Fig. 1d).¹⁹

Structure of [Zn₂Cl₂(m -pdtz)(4,4'-bipy)]_n (2**).** The single-crystal X-ray diffraction study reveals that **2** crystallizes in the triclinic space group $P\bar{1}$. The basic structure of **2** contains a 2D **sql** layer built from rhombic tetrameric {Zn₄} clusters as SBUs. The basic structural unit of **2** contains two Zn²⁺ ions, one m -pdtz²⁻ ligand, one 4,4'-bipy ligand and one Cl⁻ ion. The asymmetric unit and coordination mode of Zn²⁺ centers are shown in Fig. 2a. The two Zn²⁺ ions exhibit the same tetra-coordinated mode but different coordinated environment. They all coordinate with two different nitrogen atoms originating from two independent m -pdtz²⁻ ligands, one nitrogen atom deriving from one 4,4'-bipy ligands, and one terminal Cl⁻ to form distorted tetrahedral geometries. The only difference is the coordinated N location of m -pdtz²⁻ ligands: one Zn²⁺ ion links to two μ -1 N-donors and the other connects to two μ -3 N-donors. The bond lengths and angles are shown in Table S2.† All m -pdtz²⁻ ligands possess the same quadridentate coordination mode (μ -1,3:1',3'), *i.e.*, 1,3-N-donor from two tetrazolate groups coordinates with four different Zn²⁺ ions. Based on this coordination mode, four different Zn²⁺ ions are linked together by four m -pdtz²⁻ ligands to form a rhombic tetrameric {Zn₄} ring as SBU (see Fig. 2b). The {Zn₄} rings as SBUs are further linked by other m -pdtz²⁻ and 4,4'-bipy ligands to give a 2D layer structure (see Fig. 2c). If the rhombic {Zn₄} rings can be considered as 4-connected nodes linking with other four tetrameric {Zn₄} rings *via* m -pdtz²⁻ ligands and 4,4'-bipy ligands, the 2D framework of **2** can be rationalized as a uninodal 4-connected **sql** topology with the Schläfli symbol of {4⁴·6²} (TD10 = 221) (see Fig. 2d).¹⁹

Structure of [Zn₂(OH)₂(m -pdtz)]_n (3**).** Single-crystal X-ray diffraction analysis shows that compound **3** crystallizes in the

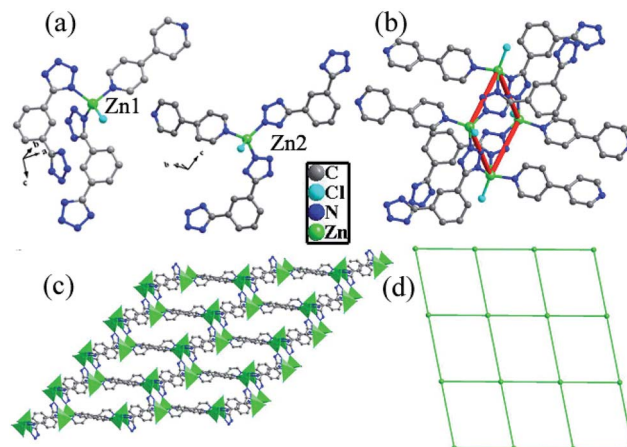


Fig. 2 (a) The ball-and-stick view of the coordination environment of the two Zn²⁺ in **2**; (b) the rhombic tetrameric {Zn₄} ring SBU in **2**; (c) the 2D layer structure of **2**; (d) the schematic view of the **sql** topology for **2**. Codes: blue, N; gray, C; green, Zn; turquoise, Cl (the hydrogen atoms have been omitted for clarity).

monoclinic space group $P2_1/c$ and exhibits a new (4,6)-connected 3D structural topology constructed from rod-shaped 1D Zn-chains as SBUs. In the asymmetric unit of **3**, there are two Zn²⁺ ion centers, two OH⁻ groups and one m -pdtz²⁻ ligand. The two Zn²⁺ ions exhibit the same tetra-coordinated mode but different coordinated environment (see Fig. 3a). They all coordinate with two different nitrogen atoms originating from two independent m -pdtz²⁻ ligands and two oxygen atoms deriving from two different OH⁻ groups to form distorted tetrahedral

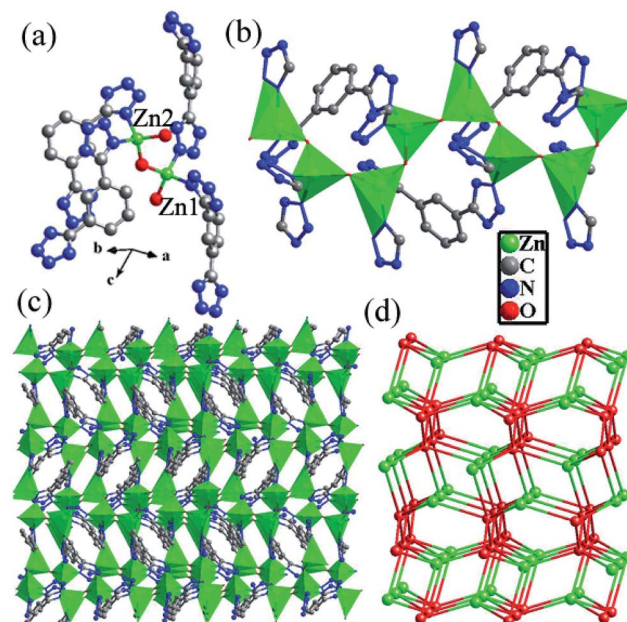


Fig. 3 (a) The ball-and-stick view of the coordination environment of Zn²⁺ in {Zn₂} cluster; (b) the polyhedral view of 1D rod-shaped Zn-chain; (c) the 3D framework in **3**; (d) the schematic view of the (4,6)-connected topology. Codes: blue, N; gray, C; green, Zn; red, O (the hydrogen atoms have been omitted for clarity).

geometries. The only difference is the coordinated N location of $m\text{-pdtz}^{2-}$ ligands: one Zn^{2+} ion links to two $\mu\text{-1}$ N-donors and the other connects to one $\mu\text{-1}$ N-donor and one $\mu\text{-2}$ N-donor. The bond lengths and angles are shown in Table S3.† So all the $m\text{-pdtz}^{2-}$ ligands adopt the same quadridentate coordination mode ($\mu\text{-1,1} : 1',3'$), in other words, one tetrazolate group coordinates with two different Zn^{2+} ions using its 1,1-N-donors and the other tetrazolate group coordinates with the other two Zn^{2+} ions using its 1,3-N-donors. At the same time, the OH^- group links to two different Zn^{2+} ions to give a binuclear $\{\text{Zn}_2\}$ cluster as SBU. Based on this coordination mode, all binuclear $\{\text{Zn}_2\}$ clusters are linked by $m\text{-pdtz}^{2-}$ ligands to form a 1D rod-shaped Zn chain (see Fig. 3b). The Zn chains are further linked together by other $m\text{-pdtz}^{2-}$ and OH^- groups to give a 3D framework (see Fig. 3c). From the topological point of view, the binuclear $\{\text{Zn}_2\}$ clusters can be abstracted as 6-connected nodes that link with other six binuclear $\{\text{Zn}_2\}$ clusters *via* $m\text{-pdtz}^{2-}$ ligands and OH^- groups, while the $m\text{-pdtz}^{2-}$ ligands can be rationalized as 4-connected nodes linking with four different binuclear $\{\text{Zn}_2\}$ clusters. Based on this simplification, the overall 3D network of **3** can be rationalized as a new binodal (4,6)-connected topology with the Schläfli symbol of $\{4^4 \cdot 6^2\}_1\{4^6 \cdot 6^9\}$ (TD10 = 1413) (see Fig. 3d).¹⁹

By careful analysis we can see that there are several $\pi\text{-}\pi$ stacking interactions in these three compounds. The face-to-face $\pi\text{-}\pi$ stacking can be found between aromatic rings. These interactions are characterized by centroid to centroid distances of 3.759(3), 3.797(3), 3.799(3) Å for **1**, 3.640(2), 4.065(2) Å for **2** and 3.916(5) Å for **3**, respectively. The detailed data are shown in Fig. S7–S9 and Table S1 (ESI†).

Fluorescence properties

The coordination polymers constructed from d^{10} metal ions and conjugated organic ligands are promising candidates for hybrid photoactive materials with potential applications such as light-emitting diodes (LEDs).²⁰ So the fluorescence properties of free ligand $m\text{-H}_2\text{pdtz}$, **1**, **2** and **3** were investigated in the solid state at room temperature. As shown in Fig. 4, the free ligand $m\text{-H}_2\text{pdtz}$ exhibits an emission maximum at 473 nm, which can be ascribed to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ electronic transition,^{16b} while the emission spectra of **1**, **2** and **3** all exhibit similar intensities of fluorescent emissions with the maxima appearing at 326 nm, thus exhibiting a large blue shift as compared with free ligand $m\text{-H}_2\text{pdtz}$.^{16b} In order to understand the nature of these emission bands, we compared the emission spectra of the three compounds and that of free organic ligands. The comparisons reveal that the free 4,4'-bipy ligand exhibits an emission maximum at 437 nm in consistence with that reported in the references,²¹ while the similar emission intensities and spectroscopic blue shifts of the CPs **1–3** can be tentatively attributed to the cooperative effects of the charge transfer process and intraligand transition of the Zn-modified $m\text{-pdtz}^{2-}$ ligands ($\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$), as reported for other Zn^{II} CPs with N-donor ligands.²² In other words, when the ligands coordinated to metal Zn^{II} centres, they can effectively increase both the rigidity

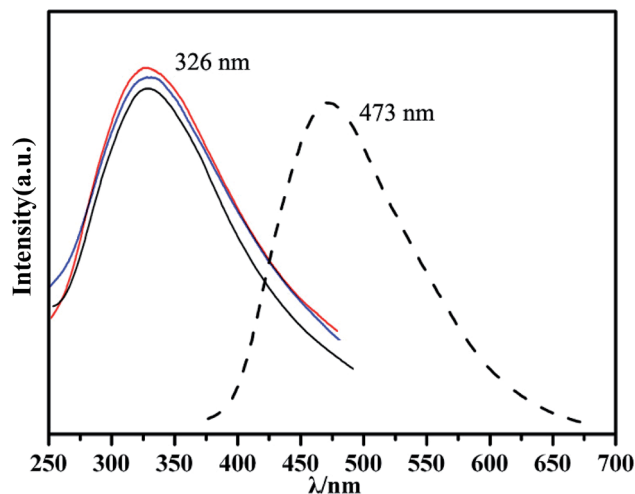


Fig. 4 The emission spectra of free ligand $m\text{-H}_2\text{pdtz}$ (black dash line), **1** (black solid line), **2** (red solid line), and **3** (blue solid line) in the solid state at room temperature.

and conjugation on CPs and then affect the energy loss *via* a radiationless pathway within the intraligand.²³

The fluorescence decays for **1–3** in the solid state at room temperature (296 K) were also investigated and obeyed double-exponential decay laws as shown in Fig. S11–S13 (ESI†). The fluorescence lifetime values of the three compounds are $\tau_1 = 1.945 \mu\text{s}$ (93.8%), $\tau_2 = 9.51 \mu\text{s}$ (6.2%) for **1**, $\tau_1 = 0.8847 \mu\text{s}$ for **2**, and $\tau_1 = 0.8031 \mu\text{s}$ for **3**, respectively. The short lifetime due to the $3d^{10}4s^0$ electron configuration of $\text{Zn}(\text{II})$ might reduce the radiative lifetime of triplets by increased spin-orbit coupling and the presence of $\text{Zn}(\text{II})$ will also facilitate intersystem crossing.²⁴

Conclusions

In conclusion, three new CPs have been constructed by an *in situ* ditetrazolate-ligand synthesis system involving the Sharpless $[2 + 3]$ cycloaddition reaction between IPN and NaN_3 in the presence of Zn^{2+} ions as Lewis-acid catalysts under hydro/solvothermal conditions. CP **1** exhibits a new 6-connected 3D structural topology constructed from dimeric $\{\text{Zn}_2\}$ clusters as SBUs. CP **2** represents a 2D **sql** structural feature built from rhombic tetrameric $\{\text{Zn}_4\}$ rings as SBUs, while CP **3** displays a new (4,6)-connected 3D structural topology constructed from rod-shaped 1D Zn-chains as SBUs. Moreover, the fluorescence properties of the three CPs have also been studied. Further investigations are underway, including the exploration of their other potential properties and an extension of the *in situ* ditetrazolate synthesis, aiming at synthesizing novel compounds with diverse topological structures and various interesting functions.

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