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A 2-D tetrazole-based Zn(II) coordination polymer: crystal structure, dielectric constant, and luminescence

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A 2-D tetrazole-based Zn(II) coordination polymer: crystal structure, dielectric constant, and luminescence

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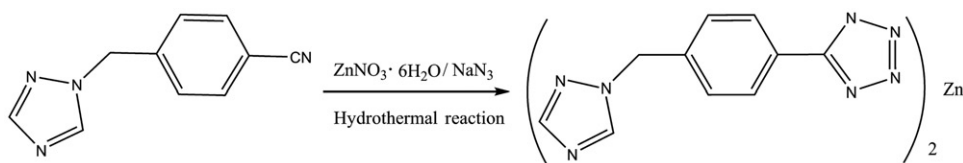
A tetrazole-based Zn(II) coordination polymer, $[\text{Zn}(\text{TMPT})_2]_n$ (**1**) (TMPT = 5-(4-((1H-1,2,4-triazol-1-yl)methyl)phenyl)-2H-tetrazole), was synthesized by *in situ* reaction of 4-((1H-1,2,4-triazol-1-yl)methyl)benzotrile, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and NaN_3 under hydrothermal conditions and structurally characterized by single-crystal X-ray diffraction. Complex **1** contains π - π stacking interactions between tetrazole rings and phenyl rings of the 2-D ordered layered structural framework, which contribute to the dielectric response. In addition, **1** was demonstrated to display strong blue fluorescence emissions in the solid state at room temperature.

Keywords: Zn(II) complex; Tetrazole; Dielectric constant; Fluorescence; π - π Stacking

1. Introduction

Design of a metal–organic framework *via* selection of metals and multifunctional ligands is attractive due to their fascinating structural diversities and potential applications as functional materials [1–14]. The tetrazole has found a wide range of applications in coordination chemistry as ligands, in medicinal chemistry as a metabolically stable surrogate for carboxylic acid groups, and in material science as high-density energy materials [15]. Of interest to supramolecular chemists is the coordination ability of the tetrazolyl through the four nitrogen donors that allows it to serve as a multidentate or bridging building block in supramolecular assemblies [16]. Sharpless and his coworkers [17] developed a new, safe, and convenient method for the synthesis of 5-substituted-1H-tetrazoles through [2 + 3] cycloaddition of organic nitriles and azide salt using Lewis acid catalyst. The *in situ* generation of bridging ligands through hydrothermal techniques has proven to be a powerful approach for the synthesis of coordination polymers as high-quality single crystals [18]. To construct high-dimensional metal–tetrazolate materials, a good strategy is to utilize different functional groups to functionalized tetrazolate, such as carboxylate, amino and pyridyl, introduced in 5-substituted tetrazoles and derivatives, making coordination chemistry

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Scheme 1. Synthesis of compound 1.

of tetrazoles more abundant and complicated [19]. In this context we used $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as a Lewis acid to conduct the [2 + 3] cycloaddition *in situ* between organic nitriles and azide salt to synthesize a bifunctional ligand simultaneously containing triazole and tetrazole groups, as shown in scheme 1, 5-(4-((1H-1,2,4-triazol-1-yl)methyl)phenyl)-2H-tetrazole (TMPT) which is used in the assembly of metal complexes. In this article, we report the synthesis, structure, dielectric constant, and luminescent properties of a 2-D coordination polymer, $[\text{Zn}(\text{TMPT})_2]_n$ (**1**).

2. Experimental

2.1. Materials and physical measurements

Chemicals and solvents were commercially obtained from Aldrich and used without purification. Infrared (IR) spectra were recorded on a SHIMADZU IRprestige-21 FTIR-8400S spectrometer in the spectral range $4000\text{--}400\text{ cm}^{-1}$, with potassium bromide pellets. The solid-state fluorescence spectra were recorded on a SHIMADZU RF-5301PC. Powder X-ray diffraction (XRD) data were collected with a Siemens D5005 diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). UV absorption was measured at room temperature using a SHIMADZU UV-2450 UV-VIS spectrophotometer. Dielectric constant was conducted using an automatic impedance TongHui2828 Analyzer with frequency of 20 Hz to 1 MHz, and pellet sample was made through a pressure of 8.0 MPa. Thermogravimetric analyses (TGA) were performed on a TGA V5.1A Dupont 2100 instrument heating from room temperature to 740°C under N_2 with a heating rate of $20^\circ\text{C min}^{-1}$.

2.2. Preparation of **1**

TMBN (1 mmol, 0.18 g), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 0.29 g), and NaN_3 (3 mmol, 0.19 g) were placed in a thick Pyrex tube (*ca* 20 cm in length). After addition of water (2 mL) and ethanol (1 mL), the tube was frozen with liquid N_2 , evacuated under vacuum and sealed with a torch. The tube was heated at 120°C for 3 days, after slow cooling to room temperature, colorless block crystals were obtained in 56% yield based on TMBN. TMBN was prepared by the method reported in the literature [20]. IR spectrum of **1**: 3124(m), 3084(m), 3041(m), 3001(m), 2947(w), 1529(s), 1450(s), 1349(m), 1321(m), 1280(s), 1247(m), 1236(m), 1109(s), 1032(m), 997(m), 943(w), 905(w), 862(m), 825(m), 742(s), 705(m), 669(m), 634(m). Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{N}_{14}\text{Zn}$ (%): C, 46.39; H, 3.11; N, 37.87. Found (%): C, 46.31; H, 3.08; N, 37.75.

Table 1. Selected bond lengths (Å) and angles (°) of **1**.

Zn(1)–N(2) ⁱⁱⁱ	1.972(2)	Zn(1)–N(2)	1.972(2)
Zn(1)–N(6) ⁱ	2.001(2)	Zn(1)–N(6) ⁱⁱ	2.001(2)
N(2) ⁱⁱⁱ –Zn(1)–N(2)	109.61(14)	N(2) ⁱⁱⁱ –Zn(1)–N(6) ⁱ	108.40(9)
N(2)–Zn(1)–N(6) ⁱ	108.66(9)	N(2) ⁱⁱⁱ –Zn(1)–N(6) ⁱⁱ	108.66(9)
N(2)–Zn(1)–N(6) ⁱⁱ	108.40(9)	N(6) ⁱ –Zn(1)–N(6) ⁱⁱ	113.06(14)
N(3)–N(2)–Zn(1)	126.03(19)	N(1)–N(2)–Zn(1)	122.32(18)
C(9)–N(6)–Zn(1) ^{iv}	128.71(19)	C(10)–N(6)–Zn(1) ^{iv}	128.2(2)

Symmetry transformations used to generate equivalent atoms: ⁱ0.5 – x, 0.5 – y, –0.5 + z; ⁱⁱ–0.5 + x, 0.5 – y, –z; ⁱⁱⁱ–x, y, –0.5 – z; ^{iv}0.5 – x, 0.5 – y, 0.5 + z.

2.3. Single-crystal XRD measurements

Crystal data for **1**: C₂₀H₁₆N₁₄Zn, M = 517.84, orthorhombic, *Pbcn*, *a* = 16.579(2) Å, *b* = 9.5355(11) Å, *c* = 13.8432(18) Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, *V* = 2188.5(5) Å³, *Z* = 4, *F*(000) = 1056, GOF = 1.120, *R*₁ = 0.0495, *wR*₂ = 0.1193 [*I* > 2σ(*I*)]. Data collection of **1** was performed with Mo-Kα radiation (λ = 0.71073 Å) on a Rigaku SCXmini diffractometer by the ω scan technique at room temperature. The structure was solved by direct methods and refined with full-matrix least-squares using SHELXTL-97 [21]. All non-H atoms and hydrogens were refined anisotropically. Hydrogens were placed in geometrically idealized positions and constrained to ride on their parent atoms with *U*_{iso}(H) = 1.2*U*_{eq}. Selected bond distances and angles are given in table 1.

3. Results and discussion

3.1. Spectral properties

In the IR spectrum of **1**, a diagnostic peak of the cyano group at 2200 cm^{–1} disappeared and peaks at 1529 and 1450 cm^{–1} emerged, suggesting the formation of a tetrazole group, in good agreement with our previous studies [16, 19a].

UV spectra of the ligand and **1** studied in the solid state at room temperature (Supplementary material) show that both the ligand and complex exhibit absorption bands at 200–400 nm. After coordination, the absorption peaks slightly red shift, owing to the formation of the large conjugated system, consisting of phenyl rings and tetrazole rings. The spectral analyses are consistent with the crystal structure.

3.2. Powder XRD pattern

The agreement between the experimental and simulated XRD patterns indicate the phase purity of **1** (figure 1). The difference in reflection intensities between the simulated and experimental patterns was due to the variation in preferred orientation for the powder sample during collection of the experimental XRD data.

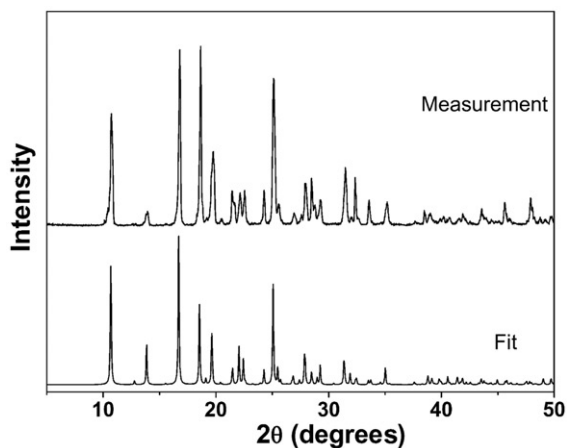


Figure 1. Powder XRD pattern of **1** where the lower line is single-crystal diffraction-simulated pattern.

3.3. Description of the crystal structure

Single-crystal X-ray analysis reveals that **1** crystallized in the orthorhombic, group *Pbcn*. The asymmetric unit of **1** consists of one crystallographically independent Zn(II) and two deprotonated TMPT ligands. The coordination environment of **1** with atomic labeling is shown in figure 2. The Zn coordinates to four nitrogens, two equivalent (N2, N2ⁱⁱⁱ) are from the tetrazole ring and the other two (N6ⁱ, N6ⁱⁱ) are from the triazole ring. [Symmetry codes: ⁱ $0.5 - x, 0.5 - y, -0.5 + z$; ⁱⁱ $-0.5 + x, 0.5 - y, -z$; ⁱⁱⁱ $-x, y, -0.5 - z$]. The geometry around Zn is slightly distorted tetrahedral. The angles at Zn fall in the range 108.40(9)–113.06(14)°. The bond lengths of Zn1–N2 and Zn1–N6 are 1.972(2) and 2.001(2) Å, respectively, comparable to those found in tetrazole-based tetrahedral Zn coordination polymers with the same coordination mode [16, 22]. The tetrazole rings and phenyl ring are nearly coplanar, the dihedral angle between two planes (the tetrazole rings and phenyl ring) is about 5.136(77)°. The dihedral angle between the triazole ring planes and phenyl ring planes is about 72.189(86)°.

From a topological perspective, each Zn may be considered as a four-connecting node, which links equivalent four-connecting centers through bridging TMPT. Since each of these ligands is only two-connecting, they are only considered as connections and not nodes. Consequently, this results in the formation of a 2-D wavy sheet with (4,4) topology (figures 3 and 4). The 2-D network structure consists of distorted rhombic grids in which the Zn···Zn distance bridged by TMPT is 11.7307(9) Å, the torsion angle of Zn···Zn···Zn···Zn in rhombic grids is 43.240(3)°. Moreover, π – π stacking interactions are found between tetrazole rings and phenyl rings with centroid–centroid separations of 3.770 Å (figure 5). The intermolecular interactions induce the 2-D sheet to a 3-D overlapped array, suggesting that π – π interactions stabilize the extended structure.

The Zn(II) adopts a tetrahedral coordination with four nitrogens, which has been observed in a few crystal structures of bistriazole-based complexes [23]. Recently 1-D zigzag chain and 1-D double chain zinc coordination polymers with btp ligand (btp = 1, 3-bis(1,2,4-triazol-1-yl)propane) have been reported, respectively, by Zhu *et al.* [24] and Feng *et al.* [25]. In order to balance valence state, anions (ClO₄⁻, BF₄⁻, NCS⁻, [N(CN)₂]⁻) were usually added as auxiliary ligands. As a result, they can behave either as a guest

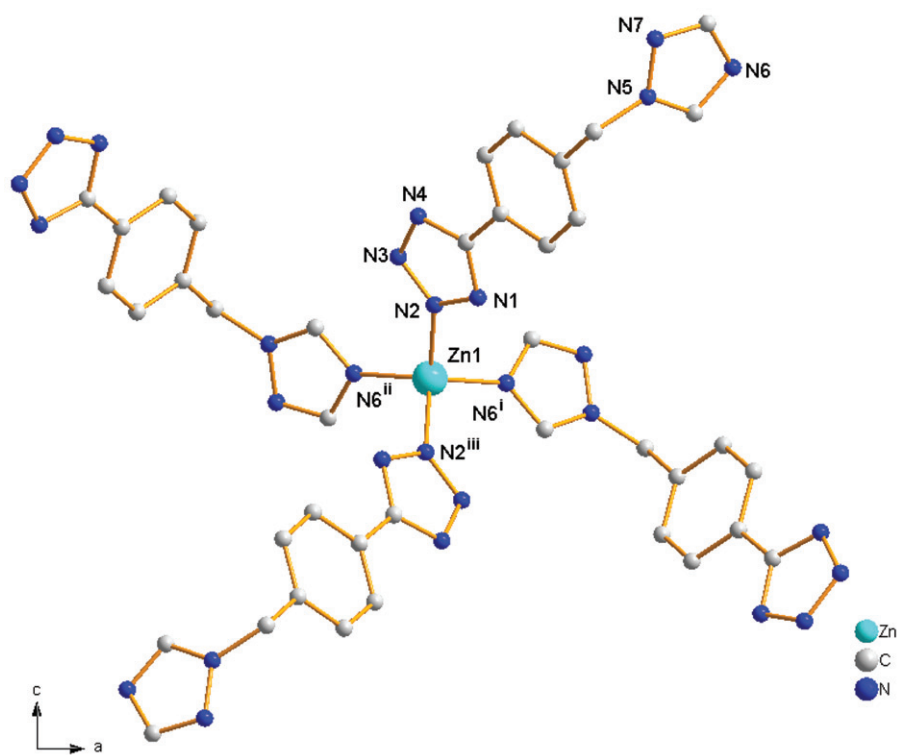


Figure 2. View of the coordination environment of Zn(II) in 1. Symmetry codes: ⁱ $0.5 - x, 0.5 - y, -0.5 + z$; ⁱⁱ $-0.5 + x, 0.5 - y, -z$; ⁱⁱⁱ $-x, y, -0.5 - z$.

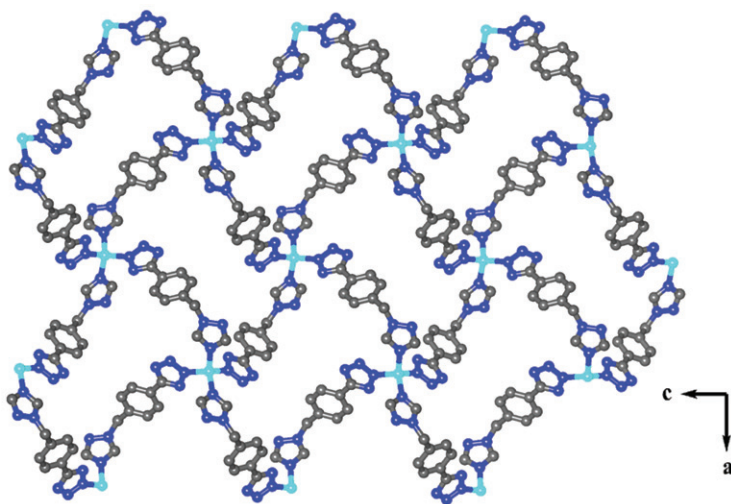


Figure 3. View of the 2-D network structure of 1.

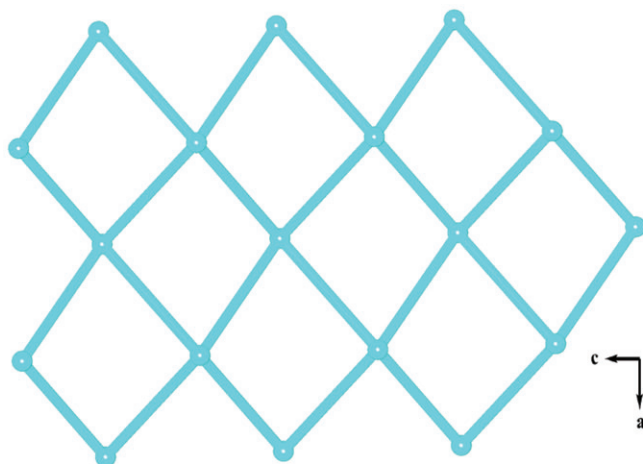


Figure 4. Schematic description of the (4,4)-connected 2-D network of **1**.

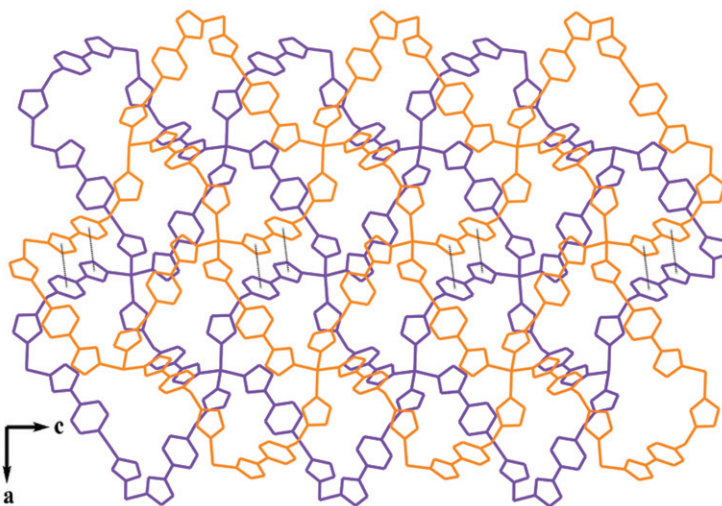


Figure 5. The 3-D supramolecular architecture *via* π - π stacking interactions of **1**.

species to fill in the cavities or as coligands forming mixed-ligand metal complexes. However, in **1**, no anions (NO_3^- and N_3^-) or solvent as auxiliary ligands take part in coordination; Zn only coordinates to four nitrogens from TMPT. The tetrazole easily deprotonates *in situ* hydrothermal method, coordinating with metal ions in the construction of metal-organic frameworks [26]. This suggests that we can construct porous materials and avoid anions in the cavities through selecting tetrazole ligands [11, 27].

3.4. Fluorescence

Aromatic organic molecules, organic polymers, and mixed inorganic-organic hybrid coordination polymers have been investigated for fluorescence and applications as

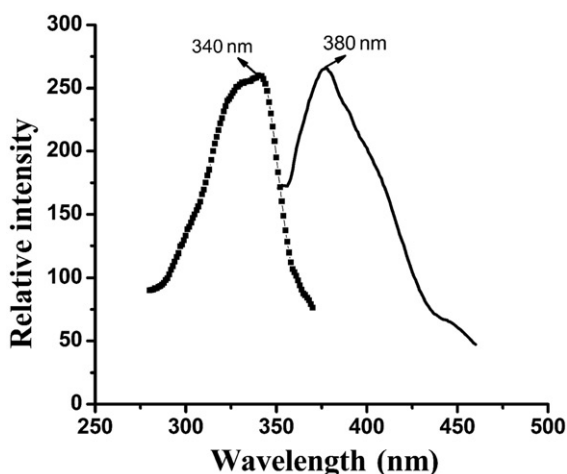


Figure 6. Fluorescent emission spectrum of **1** in the solid state at room temperature (the left spectrum is an excitation spectrum).

fluorescence-emitting materials [28]. Organic materials affect wavelength emissions such that the syntheses of inorganic–organic coordination polymers by judicious choice of organic spacers and metal centers (Zn, Cd, Pb, Ca, B, etc.) can be an efficient method to obtain luminescent materials [29]. Of particular interest is the photoluminescent spectra of powdered **1**, as shown in figure 6, the solid-state fluorescence spectra of **1** at room temperature reveal maximal emission peaks at 380 nm (with $\lambda_{\text{ex}} = 340$ nm), suggesting that **1** may be a good blue-light-emitting material. The photoluminescent mechanism is tentatively attributed to ligand-to-ligand transitions, in reasonable agreement with the literature examples on this class of metal complexes [13, 16].

3.5. Permittivity property

Research on new dielectric constant (ϵ) materials has attracted increasing interest because of their potential applications in resonators, filters, and other key components in microwave communication systems [30]. Much of the attention in this field has focused on developing inorganic dielectric material [31, 32]. In contrast, studies toward developing dielectric materials based on organic and metal–organic compound (MOC) have remained sparse [33]. Recently, our group has done research on hybrid inorganic–organic dielectric materials. Compounds with temperature-dependent dielectric constant which rapidly fluctuates may be potential phase transition, piezoelectric, ferroelectric materials [34–37].

The complex permittivity ($\epsilon = \epsilon_1 - i\epsilon_2$, in which ϵ_1 and ϵ_2 are the corresponding real and imaginary parts of the dielectric constant and dielectric dissipation factor $D = \tan\delta = \epsilon_2/\epsilon_1$) of powdered samples of **1** in the form of pellets were measured with a Tonghui TH2828A. The frequency dependence of permittivity was taken at room temperature as shown in figure 6; ϵ_1 at a lower frequency reaches a maximum value 9 (200 Hz), which drops to 4 at a relatively higher frequency of 1 MHz. This behavior is similar to that found for the perovskite-related oxide $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ [38] and the

previously reported homochiral zinc-quinene coordination polymer [39]; both show a significant decline. Dielectric dissipation measurement reveals a similar trend (figure 7). This behavior would be supported by the presence of dipolar layer vibration [40], in agreement with the presence of π - π stacking interactions between tetrazole rings and phenyl rings of 2-D layered structural framework. Dipolar layer vibration relaxation at low frequencies would be consistent with the direction change of alternating electric field (AEF). However, in the higher frequencies, the dipole reversal cannot keep up with the AEF frequency change, so the ϵ_1 values become smaller gradually with the increase in frequency, and tend to remain unchanged at higher frequencies [38]. The temperature dependence of the dielectric constant at different frequency range shows that the dielectric constants (ϵ_1) gradually increase with the rise in temperature (100–375 K) as shown in figure 8. As the frequency increases from $10^4 \rightarrow 10^5 \rightarrow 10^6$ Hz, a continuous

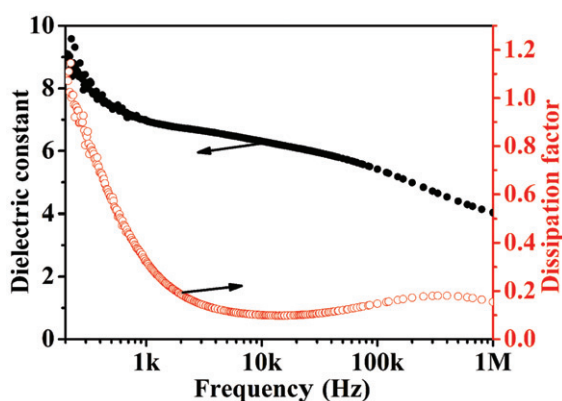


Figure 7. The dielectric constants and dielectric dissipation of frequency dependence at a frequency range of 200 Hz–1 MHz at 293 K.

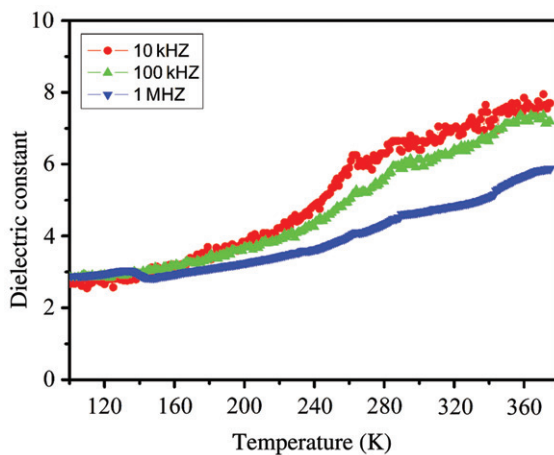


Figure 8. The dielectric constants of temperature dependence from 100 to 375 K at different frequency range (10 kHz, 100 kHz, 1 MHz).

increase in frequency results in a gradual decrease in dielectric constant. At 1 MHz, the dielectric constants (ϵ_1) have smaller change, increasing from 2.9 to 5.8 than the change from 2.9 to 7.9 at 10 kHz in the measured temperature range, consistent with the low dielectric dissipation (ϵ_2/ϵ_1) behavior at higher frequencies and further supporting the presence of a dipolar layer relaxation process.

3.6. Thermal analyses

TGA shows **1** has high stability, as shown in Supplementary material. Between 18°C and 328°C, there appeared a plateau which showed the 2-D framework was stable up to 328°C and then began to decompose with a continuous weight loss up to 690°C, showing a weight loss of 83.4% from 328°C to 690°C.

In summary, we have synthesized and structurally characterized a tetrazole-based Zn(II) coordination polymer with a wavy 2-D network. Complex **1** contains π - π stacking interactions between tetrazole rings and phenyl rings of the 2-D ordered layered structural framework, which contribute to the dielectric response. In addition, **1** displays strong blue fluorescence emissions in the solid state at room temperature, suggesting that it may be a blue-light-emitting material.

Supplementary material

CCDC 741392 contains the supplementary crystallographic data of **1** for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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