

A NOVEL 2D ZINC(II) COORDINATION POLYMER BASED ON 2,2'-BIPYRIDINE-4,4'-DICARBOXYLIC ACID: SYNTHESIS, CRYSTAL STRUCTURE AND PHOTOLUMINESCENCE PROPERTY

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Abstract. Two-dimensional Zn(II) coordination polymer $\{[\text{Zn}(\text{bpdc})(\text{H}_2\text{O})]\cdot\text{dmf}\cdot\text{H}_2\text{O}\}_n$ (**1**), where H_2bpdc = 2,2'-bipyridine-4,4'-dicarboxylic acid and dmf = *N,N*-dimethylformamide, was obtained by hydrothermal synthesis and characterized by IR spectrum and single-crystal X-ray diffraction. The Zn(II) ion is coordinated in a distorted square pyramidal N_2O_3 environment by two N-atoms from one bpdc^{2-} ligand, two carboxylate oxygen atoms from another two bpdc^{2-} ligands and one water molecule. The crystal lattice of **1** hosts the dmf and water solvent molecules via $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with crystal components. The new material reveals blue-orange luminescence upon excitation with ultraviolet light.

Keywords: zinc, 2,2'-bipyridine-4,4'-dicarboxylic acid, X-ray, luminescence.

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Introduction

The preparation of coordination polymers (CPs) is an actual topic in crystal engineering as these hybrid materials have attracted significant attention because of their intriguing architectures and topologies and are endowed with exciting physical and chemical properties, which can ultimately lead to applications [1-3]. Over the past few decades, we have been witnessing rapid development in the field of porous CPs that were subsequently designed from organic ligands and metal or cluster ions and can provide special pore environments for gas storage and separation [4].

Aromatic carboxylic acids are the most commonly used organic linkers for the self-assembly of porous CPs, and may be responsible for rich coordination modalities for the extension of metal ion into high dimensional structures. These ligands can behave as good H-bond acceptors and donors, because of the deprotonation degree and crystal packing arrangement, thus giving an additional stabilization of polymeric structures and facilitating their crystallization [5].

2,2'-Bipyridine-4,4'-dicarboxylic acid (H_2bpdc) is a bridging multidentate ligand possessing both bipyridine and carboxylate groups, making it a good candidate for the preparation of new CPs due to their diverse coordination capabilities to metal ions [6-8]. As a

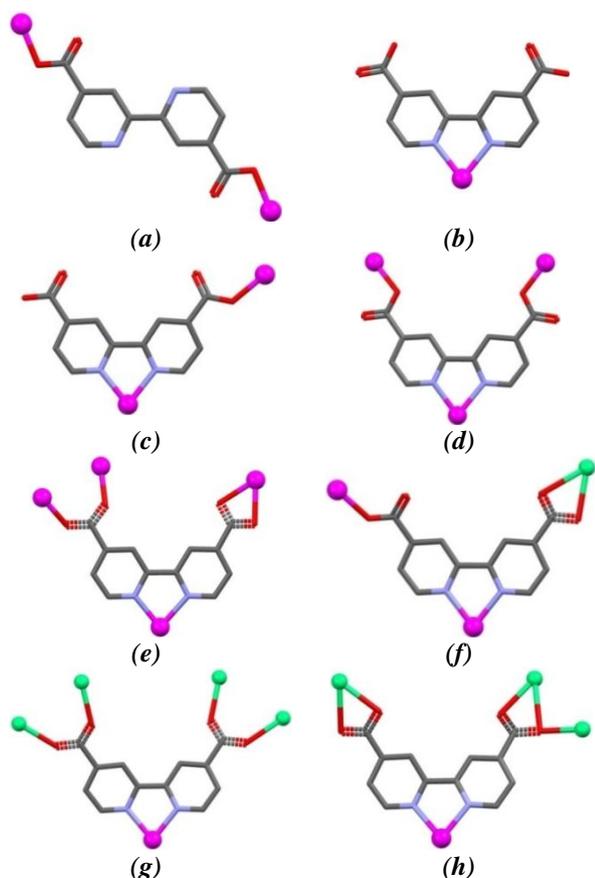
d^{10} metal ion Zn^{2+} is particularly suited for the construction of CPs. This transition metal ion easily coordinates with nitrogen and oxygen atoms, and geometries of Zn in obtained complexes can vary from tetrahedral through trigonal bipyramidal and square pyramidal to octahedral [9]. The examination of Cambridge Structural Database (CSD) [10] revealed that H_2bpdc forms homo- and heterometallic complexes with Zn(II) coordinating in bridging, chelate or/and bridging chelate modes (Scheme 1) giving rise to structural diversity, including mono- [11], pentanuclear [12] and polymeric arrays [6-8,13].

In the present paper, we report the preparation and X-ray characterization of a two-dimensional Zn(II) coordination polymer, $\{[\text{Zn}(\text{bpdc})(\text{H}_2\text{O})]\cdot\text{dmf}\cdot\text{H}_2\text{O}\}_n$ (**1**), where H_2bpdc = 2,2'-bipyridine-4,4'-dicarboxylic acid and dmf = *N,N*-dimethylformamide. Its luminescent property was investigated and discussed.

Experimental

All reagents and solvents were obtained from commercial sources and were used without further purification. The IR spectra were obtained in ATR on a FT IR Spectrum-100 Perkin Elmer spectrometer in the range of 650-4000 cm^{-1} . Emission spectra were measured for monocrystals

at room temperature on an Excitation YAG:Nd³⁺ laser, third harmonic generation, $\lambda = 337$ nm, duration of 10 ns and 10 Hz time repetition.



Scheme 1. The registered modes of bipyridine-4,4'-dicarboxylate anion coordination in the Zn(II) coordination compounds. Zn(II) atoms are shown by spheres, other transition metal atoms are shown by smaller spheres:
for mode (f) M=Nd, Sm, Eu, Tb, Dy, Er;
for mode (g) M=Gd, Tb, Dy; (h) M=Tb, Eu.

Synthesis of {[Zn(bpdc)(H₂O)]·dmf·H₂O}_n (**1**)

A mixture of Zn(BF₄)₂·nH₂O (0.024 g, 0.10 mmol), H₂bpdc (0.024 g, 0.10 mmol), NaOH (0.01 N, 1 mL), C₂H₅OH (3 mL), H₂O (3 mL) and dmf (1 mL) was put into a 8 mL Teflon-lined stainless steel container and heated at 100°C for 3 days. The resulting pink plate crystals were filtered off. Yield: ~55% (based on Zn). IR (cm⁻¹): 3735 (w), 3225 (w), 1666 (m), 1623 (s), 1556 (s), 1417 (m), 1394 (w), 1369 (s), 1291 (m), 1237 (m), 1104 (m), 1069 (m), 914 (m), 889 (m), 788 (m), 777 (m), 726 (m), 669 (w).

X-ray structure determination

Diffraction measurement for **1** was carried out at room temperature on an Xcalibur "Oxford Diffraction" diffractometer equipped with CCD area detector and a graphite monochromator utilizing MoK α radiation. Final unit cell dimensions were obtained and refined on an entire

data set. All calculations to solve the structures and to refine the proposed models were carried out with the SHELXS97 program package [14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon and oxygen atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters with Uiso(H)= 1.5 Ueq(C) and Uiso(H)= 1.2 Ueq(O), respectively. The crystallization dmf molecule is disordered over two positions (50/50% occupancy). The pictures were produced using the Mercury program [15]. The solvent accessible voids (SAVs) and Kitaigorodskii Packing Index (PI) were calculated using PLATON [16]. Crystallographic data of the new reported herein was deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 1830116.

Results and discussion

Crystal structure analysis

The complex {[Zn(bpdc)(H₂O)]·dmf·H₂O}_n (**1**) represents a chromophore, being pink coloured. Upon exposure to air, the adduct is stable in the solid state and is soluble in *N,N*-dimethylformamide. The X-ray data and the details of the refinement for compound **1** are summarized in Table 1. Selected geometric parameters are given in Tables 2 and 3.

Table 1

Crystallographic data and structure refinement details for compound 1.

Parameters	Value
Empirical formula	C ₁₅ H ₁₇ N ₃ O ₇ Zn
Formula weight	416.69
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Z	8
<i>a</i> (Å)	14.9055(19)
<i>b</i> (Å)	13.3734(9)
<i>c</i> (Å)	16.5231(7)
<i>V</i> (Å ³)	3293.7(5)
<i>D_c</i> (g/cm ⁻³)	1.681
μ (mm ⁻¹)	1.537
F(000)	1712
Crystal size (mm ³)	0.22 x 0.14 x 0.02
Reflections	7024/2899
collected/unique	[R(int)= 0.0862]
Reflections with $[I > 2\sigma(I)]$	1523
Data/restraints/parameters	2899 / 21 / 272
GOF on <i>F</i> ²	1.002
<i>R</i> ₁ , <i>wR</i> ₂ [$I > 2\sigma(I)$]	0.0683, 0.1098
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1550, 0.1361

Table 2

Selected bond distances (Å) and angles (°) in metal coordination cores in 1.			
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Zn(1)-N(1)	2.130(5)	Zn(1)-O(3) ⁱⁱ	2.034(4)
Zn(1)-N(2)	2.133(5)	Zn(1)-O(1w)	2.076(5)
Zn(1)-O(1) ⁱ	1.975(5)		
Angle	ω , deg	Angle	ω , deg
O(1) ⁱ -Zn(1)-O(3) ⁱⁱ	95.1(2)	O(1w)-Zn(1)-N(1)	163.4(2)
O(1) ⁱ -Zn(1)-O(1w)	93.1(2)	O(1) ⁱ -Zn(1)-N(2)	116.3(2)
O(3) ⁱⁱ -Zn(1)-O(1w)	94.3(2)	O(3) ⁱⁱ -Zn(1)-N(2)	147.9(2)
O(1) ⁱ -Zn(1)-N(1)	102.0(2)	O(1w)-Zn(1)-N(2)	90.4(2)
O(3) ⁱⁱ -Zn(1)-N(1)	91.4(2)	N(1)-Zn(1)-N(2)	76.7(2)

Symmetry transformations used to generate equivalent atoms: ⁱ -x+5/2, y-1/2, z, ⁱⁱ x, -y+3/2, z+1/2

Table 3

Hydrogen bond distances (Å) and angles (°) in 1.				
D-H...A	<i>d</i> (H...A)	<i>d</i> (D...A)	\angle (DHA)	Symmetry transformations for acceptor
O(1w)-H(1w1)...O(3)	1.96	2.773(6)	162	-x, y-1/2, -z+1/2
O(1w)-H(2w1)...O(2w)	1.87	2.705(8)	168	x, y, z
O(2w)-H(1w2)...O(1S)	1.93	2.77(3)	167	x, -y+3/2, z+1/2
O(2w)-H(1w2)...O(1SA)	2.25	3.06(3)	158	x, -y+3/2, z+1/2
O(2w)-H(2w2)...O(2)	1.93	2.784(7)	179	-x, y-1/2, -z+1/2

Compound **1** crystallizes in the orthorhombic centrosymmetric *Pbca* (No. 61) space group and the asymmetric unit consists of [Zn(bpdc)(H₂O)]·dmf·H₂O. In the crystal structure of the complex, the coordination environment around the Zn atom can be described as a distorted square pyramidal coordination geometry originated from two N-atoms from one bpdc²⁻ ligand, two carboxylate oxygen atoms from another two bpdc²⁻ ligands and one water molecule (Figure 1, Table 2).

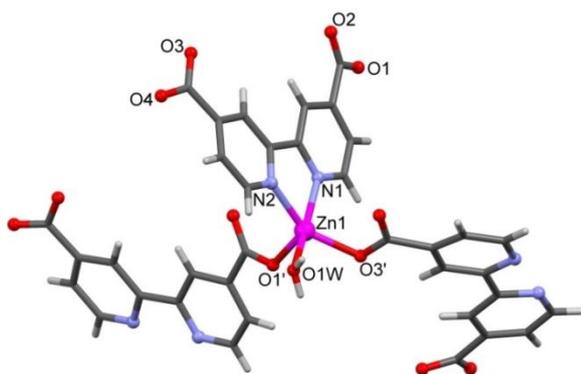


Figure 1. View of the coordination environment of the Zn(II) ion in 1 with the partial numbering scheme.

The Zn(II) square pyramidal coordination polyhedron geometry is confirmed by the general descriptor $\tau = (\beta - \alpha)/60$, where α and β , being the two largest angles at the metal center for five-

coordinated complexes [17], adopt the value of 0.114. Each bpdc²⁻ ligand chelates to one Zn(II) site through the pyridyl nitrogen donors and links two adjacent Zn(II) ions by carboxyl groups, resulting in a 2D wave-like layer (Figure 2(a)). The chelation of the Zn(II) ion to the 2,2'-bipyridine site of the bpdc²⁻ ligand restrains the planar conformation of the bipyridyl rings, as indicated by its dihedral angle (9.21°).

The polymeric structure of complex **1** is best described as a 2D wave-like network with (4,4) or 4⁴ topology [18] and was observed in the *bc*-plane, and the Zn...Zn distances are 8.941 and 9.056 Å along the *c*- and *b*-axes, respectively. The layers are further interlinked by O-H...O hydrogen bonds between coordinated water molecules and bpdc²⁻ to afford a 3D supramolecular framework. The crystallization water and dmf molecules are accumulated in the crystal lattice via O-H...O hydrogen bonds: the solvate water molecules are binding with the coordinated water molecule as the acceptor, and with the O atom of carboxylic group as the donor, while dmf molecules are binding only with uncoordinated water molecules (Table 3). The volume, occupied by solvent molecules as calculated by PLATON comprises 1092.6 Å³ or 33.2% of the total unit cell volume, thus indicating a high solvent uptake (Figure 2(b)).

Analysis of the Cambridge Structural Database [10] reveals 3 Zn(II) homonuclear coordination polymers (Table 4) built up from

bpdc anions and no other co-ligand with the Zn(II) atoms being in the N_2O_3 square pyramidal [18] and N_2O_6 octahedral coordination environments [19,20]. Similar to **1**, in two 3D coordination polymers bpdc ligand coordinates in bis-chelate mode to one metal center and bis-bridging mode to two adjacent Zn(II) ions

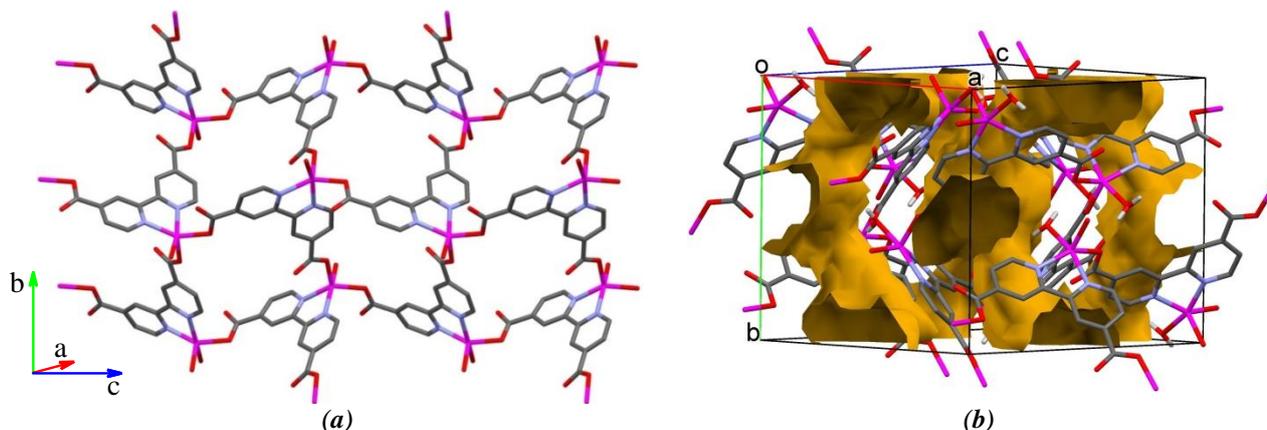


Figure 2. View of the fragment of the (4,4) coordination layer (a) and of the solvent accessible area in **1** (b).

Table 4

Selected geometrical and crystal packing parameters in **1** and relative compounds.

Compound	Space group	Topology	PI, %	SAVs, Å ³ (%)	Reference, refcode in CSD
{[Zn(bpdc)(H ₂ O)]·dmf·H ₂ O} _n (1)	Pbca	2D	74.1	1092.6 (33.2) ^a	Present work
{[Zn(bpdc)(dmf)]·dmf} _n	P2 ₁ /n	3D	71.3	591.2 (29.6) ^a	[8], COTYER
[Zn(bpdc)(H ₂ O) ₂] _n	P3 ₁ 2 ₁	3D	67.7	–	[19], PASGEX
{[Zn(bpdc)(H ₂ O) ₃]·3(H ₂ O)} _n	P2 ₁ /c	1D	72.8	146.9 (9.1) ^a	[20], SADTEY

^a SAVs calculated with the removal of guest molecules (H₂O and dmf).

Infrared spectroscopy study

The IR spectrum of **1** exhibits characteristic $\nu(\text{OH})$ vibrations of coordinated and lattice water molecules, observed at 3735–3225 cm^{-1} . The carboxylic groups of the bpdc²⁻ ligand give intense and medium bands resulting from asymmetric (ν_{as}) 1666 and 1556 cm^{-1} and symmetric (ν_{s}) 1394 cm^{-1} vibration modes. These bands overlap with the $\nu(\text{C}=\text{N})$ stretching vibrations of the pyridine rings. The $\nu(\text{C}=\text{C})$ ring stretching can be observed in near 1623 cm^{-1} . The medium band at 778 cm^{-1} may be attributed to the overlap of $\delta(\text{OCO})$ stretching with C–H deformation oscillations. The C–H deformation modes are presented at ~788 and 726 cm^{-1} . The presence of the dmf molecule is proved by the signals: $\delta(\text{CH}_3)$ at 1417 cm^{-1} , $\nu_{\text{as}}(\text{C}-\text{N})$ at 1266 cm^{-1} and $\nu_{\text{s}}(\text{C}-\text{N})$ at 889 cm^{-1} .

Luminescent properties

The luminescence property of compound **1** and pure H₂bpdc ligand were studied in the solid state at room temperature, $\lambda_{\text{ex}} = 337 \text{ nm}$, in the wavelength region 350–750 nm (Figure 3).

(Scheme 1(d)), while bis-chelate bridging mode coordination is observed in the third compound (Scheme 1(c)). Analyzing Table 4, we can conclude that compound **1** is the best packed with the biggest PI and demonstrates the most promising adsorptive properties with the removal of solvent molecules.

The free H₂bpdc ligand fluorescence spectrum exhibits one intensive band at 2.97 eV (417 nm).

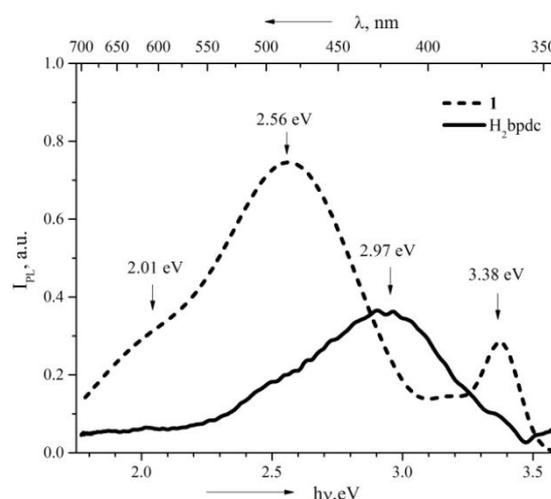


Figure 3. Solid-state luminescence emission spectra of compound **1** and free H₂bpdc ligand.

Compound **1** emits a small intensive ultraviolet fluorescence peak at 3.38 eV (366 nm) and a high intensive band with 2.56 eV (483 nm) and

2.01 eV (616 nm) shifted towards the blue-orange region of the spectra. These peaks can be observed in the H₂bpdC spectrum, but with a 4-5 fold lower intensity than in the complex, while the intensity of the violet peak at 2.97 eV is 30 times greater than in compound **1**. In comparison with the free organic ligand the integral emissions of **1** is twice higher and may be attributed to the ligand-metal interaction.

Conclusions

A new 2D Zn(II)-bpdC coordination polymer {[Zn(bpdC)(H₂O)]·dmf·H₂O}_n was prepared hydrothermally and the single crystal X-ray structure is reported. The organic 2,2'-bipyridine-4,4'-dicarboxylate anions coordinate to the metal centers in tetradentate mode and provide extension of structure. The compound represents a solvate with water and dmf solvent accumulated in the crystal lattice and reveals blue-orange emission in the solid state.

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