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Synthesis, Crystal Structure, and Fluorescence Properties of a Novel Coordination Polymer $[Zn(L)(4,4'\text{-Bipyridine})(H_2O)]_n \cdot (H_2O)_4$[1]

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Abstract—In this work, a novel and rare coordination polymer, $[Zn(L)(Bipy)(H_2O)]_n \cdot (H_2O)_4$ (H_2L—sphenylpropylmalonate acid, Bipy—4,4'-bipyridine), has been synthesized and characterized by elemental analysis, FT-IR spectroscopy, and solid fluorimetry studies. In the crystal, the Zn^{2+} ion of the complex is hexacoordinated in a slightly distorted octahedral configuration forming the unit structure, 2D structure, and 3D framework. The supramolecular architecture was constructed by a unit of $(H_2O)_4$ discrete water cluster. Besides, the coordination polymer displays strong emission spectra due to the metal-to-ligand charge-transfer transition, having potential applications as fluorescent materials.

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INTRODUCTION

In recent years, coordination polymers or supramolecular architectures with different dimensionalities have captured interest of researchers. Owing to their intriguing construction from weak interactions, such as π–π-stacking, hydrogen bonds, ion–π interaction, and hydrophobing interactions. The supramolecular compounds have become the extensive focus of magnetism, molecular absorption, catalysis, electrical conductivity, host-guest chemistry, etc. [1–5]. Meanwhile, these extended coordination polymers have molecular topological structures [6–8]. Many topological structures of coordination polymers have been constructed from the basis of N,N-bidentate ligands, such as 4,4'-bipyridine (Bipy), 2,2'-bipyridine, and 4,4'-trimethylenedipyridine [8–10]. Bipy with aromatic rings is an organic molecule with a rigid structure, with which it is suitable for emission fluorescence. Compared to organic luminescent materials, metal-organic coordination polymers have the advantages of high luminescence efficiency and excellent stability [11]. Benzenealkyl dicarboxylate shows excellent performances during and after coordination of the complexes and the potential applications in biological activity and synthesis of new drugs [12]. However, to our best of knowledge, benzenealkyl dicarboxylates as ligands are relatively less [11, 12]. Although many Zn(II) complexes have been reported, those with benzenealkyl dicarboxylate and Bipy are still surprisingly rare.

In this paper, we successfully designed and synthesized a novel coordination polymer $[Zn(L)(Bipy)(H_2O)]_n \cdot 4H_2O$ (**I**) (L—phenylpropylmalonate) including isolated $(H_2O)_4$ cluster units. The crystal structure, synthesis, and characterization are also discussed in this work.

EXPERIMENTAL

Materials and measurements. Ligand L was prepared according to a previously published method with some modifications [13]. Other chemicals were purchased from commercial sources and came into use without further purification. Element analysis (C, H, and N) were performed with a model Finnigan EA 1112 instrument. IR spectra were run as KBr pellets with a Nicolet IR-470 instrument.

Synthesis of the L. A total of 10 mL of β-phenylpropanol and 7 mL of pyridine were mixed, stirred, and heated to 65°C, and then 10 mL of thionyl chloride was added to the mixture. The mixture was stirred and heated at 115°C under reflux for 1.5 h, after which it was cooled to room temperature, and the white solid appeared. The water was added to the stirring mixture. The organic phase was separated directly from the reaction mixture with a separating funnel. The combined organic phases were dried, and the solvent was removed. The phenylpropylchlorine was separated by vacuum distillation under conditions of 142–143°C and was then added to a mixture of sodium ethoxide and dipropylmalonate (water bath at a constant temperature of 60°C) under reflux for 4 h. The phenylpropylmalonate was obtained by vacuum distillation un-

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der conditions of 172–174°C and then was hydrolyzed. After about 30 min, the white solid was obtained, extracted, and recrystallized. L was obtained in 32.4% yield. ^{1}H NMR (300 MHz, DMSO-d$_6$, δ, ppm): 1.53 (m., 2H, H3), 1.76 (m., 2H, H2), 2.52 (m., 2H, H1), 2.66 (t., 1H, $CH_2CH_2CH_2CHPh$), 7.18 (b.m., 5H, Ph).

Synthesis of complex I. The concentration of all reagents was 10 mmol L^{-1}. An aqueous solution (10 mL) containing 1 mmole of H_2L was added dropwise into 10 mL of an aqueous solution containing 1 mmole of $Zn(NO_3)_2$ with stirring and the mixture was allowed to react for 5 h at room temperature. Then 10 mL of Bipy (1 mmol) dissolved in 40% (v/v) ethanol was added, and the reaction was continued to occur for 15 h. Afterwards, the pH of the mixture was adjusted to 4.52 by the addition of an aqueous solution of HCl. Light colorless transparent solution was obtained by filtration, and the solution was filtered and kept in air. After a few days, the resulting colorless transparent crystals were obtained, and then filtered off, washed with ethanol.

IR (ν, cm^{-1}): 3428 m, 2925 m, 1719 m, 1611 s, 1582 s, 1416 s, 138 s, 1213 m, 1072 m, 811 m, 698 m, 643 m.

For $C_{22}H_{30}N_2O_9Zn$ ($M = 533.88$)

anal. calcd., %:	C, 49.49;	H, 5.66;	N, 5.25.
Found, %:	C, 49.57;	H, 5.72;	N, 5.15.

X-ray structure determination. Single-crystal data of complex **I** were collected at 293 K in a range of $1.61° < \theta < 26.04°$ on a Brucker Smart 1000 CCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å).

The structure was solved using direct methods with the full-matrix least-squares technique using the SHELXL-97 program [14, 15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from different Fourier maps. Crystal data and structure refinement for complex **I** are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2. The coordinates of the atoms and the thermal parameters were deposited with the Cambridge Crystallographic Data Centre (no. 815303; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The base structure of polymer complex **I** as shown in Fig. 1. As can be seen, the Zn^{2+} ion of complex **I** is hexacoordinated in a slightly distorted octahedral configuration. Each Zn^{2+} ion is six-coordinated by two nitrogen atoms from two Bipy molecules, three oxygen atoms from two L ligands, and one coordinated water molecule.

Besides, each L provides two oxygen atoms (O(3*A*), O(4*A*)) to bidentate chelating one Zn^{2+} ion, and each L also provides one oxygen atom (O(2)) bridging one

Table 1. Crystal data and structure refinement parameters for **I**

Parameter	Value
Empirical formula	$C_{22}H_{30}N_2O_9Zn$
Formula weight	531.85
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	11.4565(13)
b, Å	25.345(3)
c, Å	8.6199(10)
β, deg	102.898(2)
V, Å^3	2439.7(5)
Z	4
ρ_{calcd}, g cm^{-3}	1.448
Absorption coefficient, mm^{-1}	1.060
Crystal size, mm	0.10 × 0.08 × 0.06
θ Range for data collection, deg	1.61–26.04
F(000)	1112
Scan mode	φ and ω scans
Limiting indices	$-13 \le h \le 14$, $-31 \le k \le 25$, $-10 \le l \le 7$
Reflections collected/unique	11177/4754
Refinement parameters	312
Goodness-of-fit on F^2	1.036
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0650$, $wR_2 = 0.1751$
R indices (all data)	$R_1 = 0.1229$, $wR_2 = 0.2060$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	2.058 and –0.899

Table 2. Selected bond lengths (Å) and bond angles (deg) for structure **I***

Bond	d, Å	Bond	d, Å
Zn(1)–N(1)	2.201(5)	Zn(1)–N(2)$^{\#2}$	2.141(5)
Zn(1)–O(1)	2.097(4)	Zn(1)–O(2)	2.101(4)
Zn(1)–O(3)$^{\#1}$	2.067(4)	Zn(1)–O(4)$^{\#1}$	2.093(4)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(4)$^{\#1}$Zn(1)O(3)$^{\#1}$	86.22(17)	O(4)$^{\#1}$Zn(1)O(1)	86.41(17)
O(3)$^{\#1}$Zn(1)O(1)	172.55(17)	O(4)$^{\#1}$Zn(1)O(2)	166.65(17)
O(3)$^{\#1}$Zn(1)O(2)	81.48(16)	O(1)Zn(1)O(2)	105.96(17)
O(4)$^{\#1}$Zn(1)N(2)$^{\#2}$	92.85(18)	O(3)$^{\#1}$Zn(1)N(2)$^{\#2}$	89.09(18)
O(1)Zn(1)N(2)$^{\#2}$	90.19(19)	O(2)Zn(1)N(2)$^{\#2}$	92.13(18)
O(4)$^{\#1}$Zn(1)N(1)	85.67(18)	O(3)$^{\#1}$Zn(1)N(1)	90.56(18)
O(1)Zn(1)N(1)	89.97(19)	O(2)Zn(1)N(1)	89.26(18)
N(2)$^{\#2}$Zn(1)N(1)	178.5(2)		

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $x, -y + 3/2, z + 1/2$; $^{\#2}$ $x + 1, y, z$.

Zn(Bipy)(H_2O) entities including isolated $(H_2O)_4$ cluster units, resulting in a 1D chain as shown in Fig. 2.

Additionally, along x direction, the fragments of Zn(L)(H_2O) formed from L molecules and Zn^{2+} ions are in turn bridged by Bipy nitrogen atoms *via* two Zn–N coordination bonds affording a 2D structure of the complex, as shown in Fig. 3a. There is C–H···π-stacking interactions in the complex as shown in Fig. 3b.

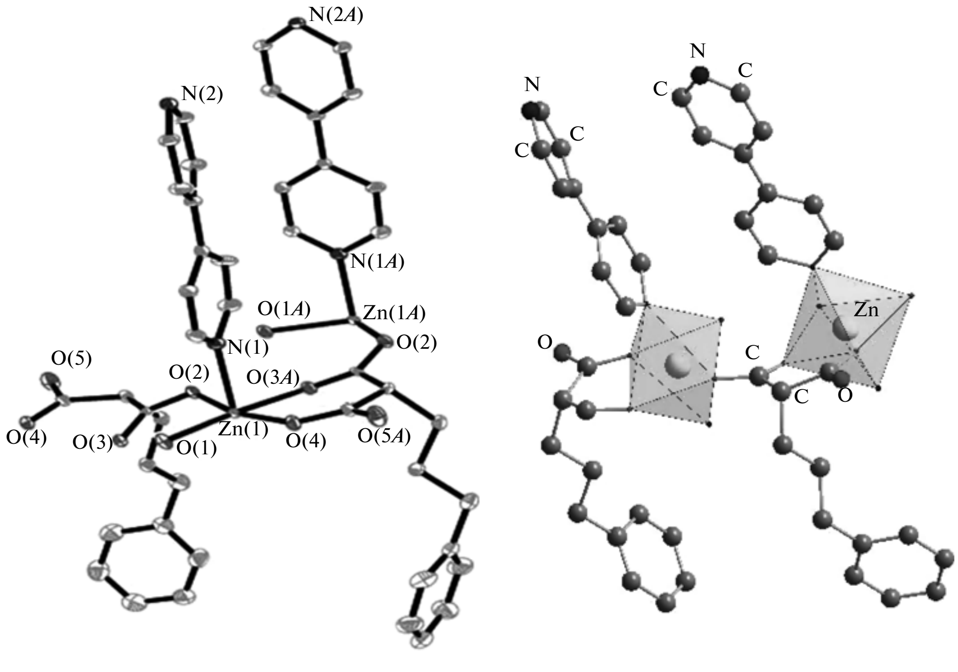

Fig. 1. Basic structure of the complex (H atoms were omitted for clarity).

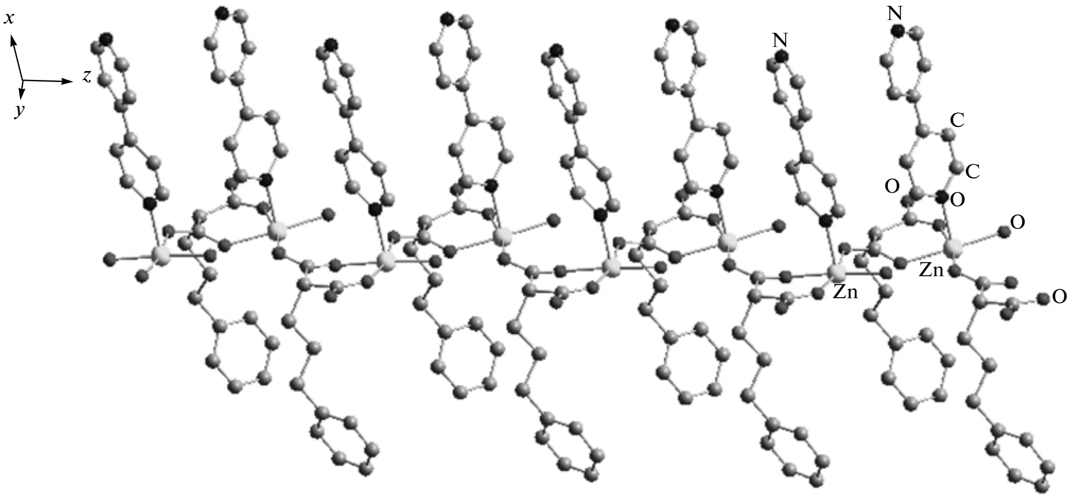

Fig. 2. 1D polymeric chain of the coordination polymer (H atoms were omitted for clarity).

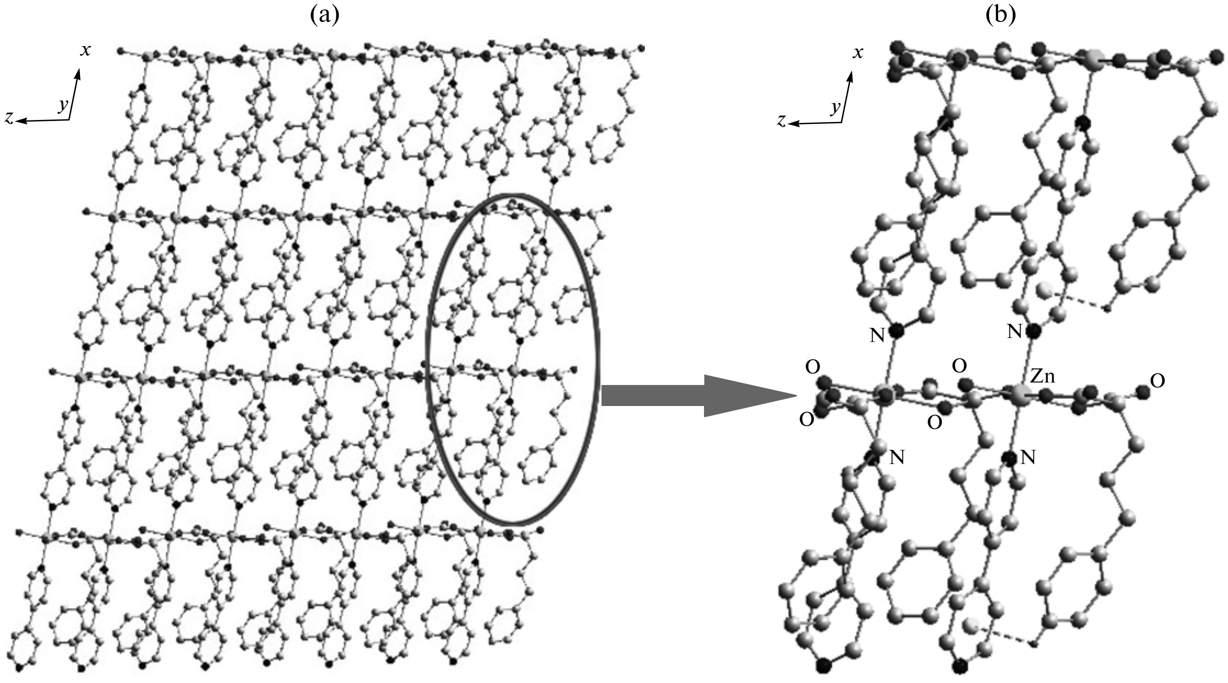

Fig. 3. 2D layer structure of the complex (a); C–H···π-stacking interactions in the complex (b). H atoms were omitted for clarity.

The distances between H(13) and the benzene ring are 3.39 Å, respectively, and these are shorter than 3.8 Å normally found for intermolecular C–H···π interactions [16, 17].

Interestingly, the presence of four lattice water molecules, one carboxyl oxygen atom, and one coordinated water molecule in each structure unit leads to a complicated hydrogen bonding system. Finally, the 2D layers were connected by hydrogen bonding interactions (as shown in Fig. 4b), forming a numerous complicated 3D stacked structure as illustrated in Fig. 4a.

It is well known that the vast H-bond network formed is based on water clusters, which often appear in the complex crystals [18–22]. In this paper, four water molecules (O(1*w*), O(2*w*), O(3*w*), and O(4*w*)) formed a discrete water cluster with the oxygen atoms, which come from L (O(5)) and coordinated water molecules (O(1)), resulting in the discrete 1D chain of water cluster formed by a unit of $(H_2O)_4$. As illustrated in Fig. 4c, the O···O distance in the water cluster of the

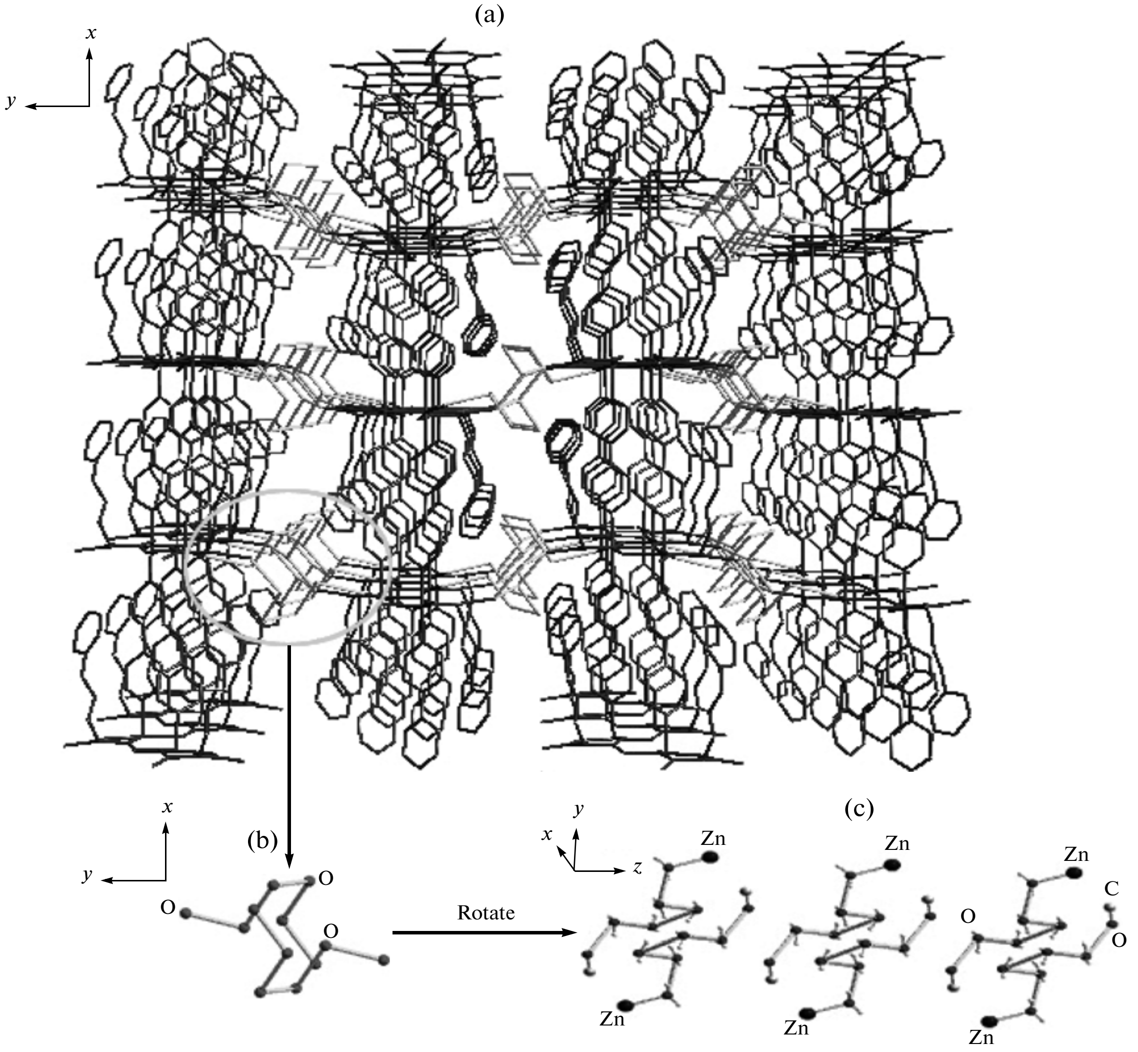

Fig. 4. 3D structure of the coordination polymer (2D layers connected by hydrogen-bonding interactions) (a); 1D chain of the discrete water cluster in complex **I** ormed by a unit of $(H_2O)_4$ in different directions (b), (c).

complex ranges from 2.618 to 2.941 Å with an average distance of 2.8 Å, which is appropriate to those observed in the ice phase (2.77–2.84 Å) and shorter than those in liquid water (2.854 Å) [23, 24].

The IR spectrum of complex **I** was observed as a broad band centered at 3428 cm^{-1} that may be assigned to O–H stretching of the water cluster [25]. The weak δ(C=O) absorption band at 1719 cm^{-1} exhibits full carboxyl group coordination modes for the metal ions [26]. The δ(C–N) peak displayed at 1213 cm^{-1} and the other strong absorption peak observed at 1161–1582 cm^{-1} can be attributed to stretching of the aromatic ring [27, 28].

The solid-state fluorescence property of a complex powder was measured at room temperature and emission spectrum is given in Fig. 5. Bipy shows fluorescence with an emission peak at 465 nm upon excitation at 369 nm. The phenylpropylmalonate (L) shows fluorescence with a weak emission peak at 305 nm upon excitation at 263 nm. The complex exhibits the fluorescence emission maximum at 545 nm upon excitation at 510 nm. Compared to the emission spectrum of Bipy (λ_{em} = 465 nm), the emission peak of complex **I** has shifted 80 nm ($\Delta\lambda_{em}$ = 80 nm). The emission of complex **I** is assigned to the ligand-to-metal charge-transfer transition [29–31].

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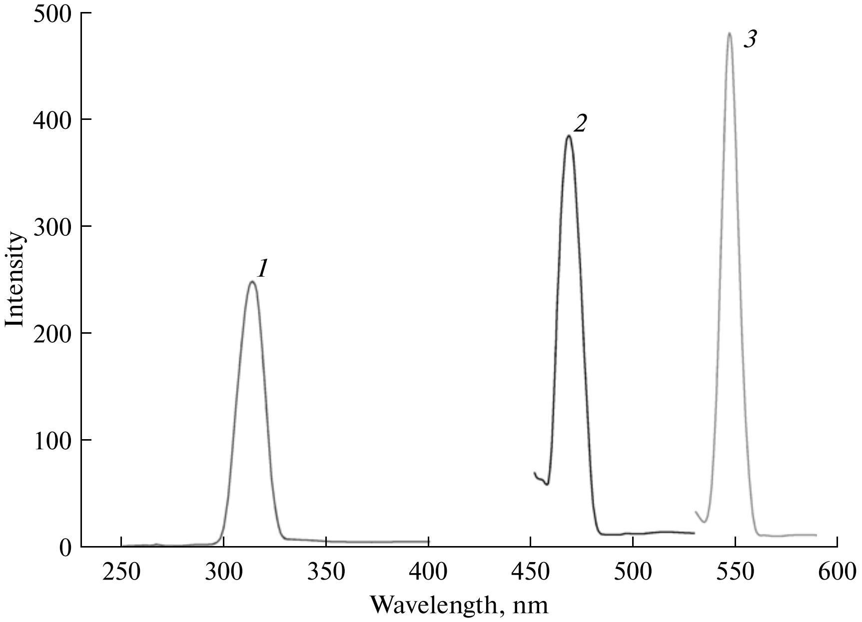

Fig. 5. Room-temperature solid-state emission spectra: L (*1*), Bipy (*2*), and complex (*3*).

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