ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2018, Vol. 44, No. 3, pp. 214–219. © Pleiades Publishing, Ltd., 2018.

Syntheses, Structures, and Properties of Two Zn(II)/Ag(I) Complexes Assembled from Tetracarboxylic Acids and N-Donor Ligands[1]

Y. P. Li[a], F. Y. Ju[b], G. L. Li[a], L. Y. Xin[a], X. L. Li[a], and G. Z. Liu[a, *]

[a] *College of Chemistry and Chemical Engineering, and Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang, 471934 P.R. China*

[b] *School of Food and Drug, Luoyang Normal University, Luoyang, 471934 P.R. China*

**e-mail: gzliuly@126.com*

Received June 21, 2017

Abstract—Two new complexes $\{[Zn(H_2L)(Bpp)] \cdot H_2O\}_n$ (**I**) and $\{[Ag(H_3L)(Bpp)] \cdot 0.25H_2O\}_n$ (**II**) (H_4L = 5-(2,3-dicarboxy phenoxy) isophthalic acid, Bpp = 1,3-bis(4-pyridyl)propane) were prepared and characterized by single crystal X-ray diffraction (XRD) (CCDC nos. 1578523 (**I**), 1578529 (**II**)), element analysis and powder XRD. Compound **I** showed a one-dimensional chain structure, in which the zinc(II) ion is four-coordinated with a tetrahedral geometry. Compound **II** is a 1D chain structure with the H_3L^- suspension arms. Complexes **I** and **II** are further extended into three-dimensional supramolecular framework via hydrogen bonds and π–π interactions. The solid state luminescent properties of compounds **I** and **II** have been investigated.

Keywords: coordination polymer, mixed ligand, fluorescence

DOI: 10.1134/S1070328418030028

INTRODUCTION

Recently, coordination polymers (CPs) have caught much attention not only due to their structural diversity but also great potential use in many areas, such as catalysis [1, 2], gas storage [3, 4], luminescence [5–7], ion exchange [8], electrochemistry [9], magnetism [10, 11], bioimaging [12], etc. Nevertheless, the construction of coordination polymers with desired structures and peculiar properties still maintains a challenge because there are so many factors affect the resulting polymers [13]. Of all factors, selection of suitable multicarboxylate ligands to metal ions of complexes is a key strategy for construction. Different metal ions have different coordination numbers, and different organic ligands adopt different coordination modes (monodentate, bridging, chelating, and so on), resulting in entirely different architecture structures [14, 15]. Moreover, when the ancillary ligands are introduced to constructed the coordination polymers, the final structures have more tunability [16]. Supramolecular interactions such as intermolecular π–π interactions and hydrogen bonding play an important role in molecular aggregation and produce novel CPs [17].

With the above consideration, the semirigid tetrahydric acid named 5-(2,3-dicarboxy phenoxy) isophthalic acid (H_4L) and auxiliary ligand 1,3-bis(4-pyridyl)propane (Bpp) were chosen for the following considerations: (1) two benzene rings of H_4L and two pyridine rings of Bpp, which potentially provide supramolecular interactions such as π–π interactions between the benzene rings to construct intriguing structures; (2) eight potential collocation points, which can afford more coordinating patterns to construct amusing coordination frameworks; (3) the introduction of additional N-donor ligands to such systems can modify the structures and properties of the resulting materials [18].

In the paper, we report the syntheses and crystal structures of two new Zinc(II)/Silver(I) complexes, namely, $\{[Zn(H_2L)(Bpp)] \cdot H_2O\}_n$ (**I**) and $\{[Ag(H_3L)(Bpp)] \cdot 0.25H_2O\}_n$ (**II**), respectively. Photoluminescence and the thermal stability of the complexes in the solid state were studied.

EXPERIMENTAL

Materials and methods. All chemicals were used as obtained without further purification. Elemental analyses for C, H and N were performed on a Vario EL III elemental analyzer. The luminescence spectra were

---

[1] The article is published in the original.

Table 1. Crystallographic data and structure refinements for **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	624.86	655.87
Temperature, K	287.94(15)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a, Å	10.0976(5)	21.425(8)
b, Å	12.3282(7)	14.113(6)
c, Å	12.5660(6)	19.008(9)
α, deg	60.749(5)	90
β, deg	87.549(4)	110.759(11)
γ, deg	85.632(4)	90
V, Å^3; Z	1360.83(12); 2	5374(4); 8
ρ_{calcd}, Kg/m^3	1.525	1.621
θ Range for data collection, deg	3.712–25.498	1.77–25.25
Reflections collected/unique	14155/4993	15825/4785
R_{int}	0.023	0.0250
Goodness-of-fit on F^2	1.068	1.048
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0285$, $wR_2 = 0.0688$	$R_1 = 0.0354$, $wR_2 = 0.0936$
R indices (all data)	$R_1 = 0.0312$, $wR_2 = 0.0704$	$R_1 = 0.0469$, $wR_2 = 0.1013$
Largest diff. peak and hole, e Å^{-3}	0.27 and −0.29	0.675 and −0.577

performed on an Aminco Bowman Series 2 Luminescence spectrometer at room temperature. The thermogravimetric (TG) analyses were carried out on a STA449C integration thermal analyzer.

Synthesis of I. A mixture $Zn(OAc)_2 \cdot 2H_2O$ (0.05 mmol, 11 mg), H_4L (0.05 mmol, 18 mg) and Bpp (0.020 g, 0.1 mmol) was dissolved in 6 mL of H_2O. The final mixture was placed in a Teflon-lined stainless-steel container, heated at 160°C for 5 days, then cooled to room temperature and the colourless block crystals suitable for X-ray analysis were obtained.

For $C_{29}H_{24}N_2O_{10}Zn$

anal. calcd., %	C, 55.74	H, 3.87	N, 4.48
found, %	C, 55.69	H, 3.91	N, 4.49

Synthesis of II. Colourless blocked crystals of **I** were grown from solvothermal reactions of $AgNO_3$ (0.017 g, 0.1 mmol), H_4L (0.018 g, 0.05 mmol) and Bpp (0.020 g, 0.1 mmol) in the solvents of H_2O in a 23 mL Teflon-lined autoclave at 120°C for 4 days. The product was washed with water and dried in the air.

For $C_{29}H_{23.5}N_2O_{9.25}Ag$

anal. calcd., %	C, 53.11	H, 3.62	N, 4.27
found, %	C, 53.15	H, 3.63	N, 4.26

X-ray crystallography. Single crystal X-ray diffractions analysis of the two complexes was carried out. Single crystal of complexes **I** and **II** was put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using φ/ω scan technique at room temperature. The structures were solved by direct methods with SHELXS-97 [19]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [20]. Table 1 shows crystallographic crystal data of compounds **I** and **II**. Selected bond lengths and angles are listed in Table 2.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1578523 (**I**), 1578529 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Structure **I** features a one-dimensional infinite coordination polymer. The asymmetric unit contains one crystallographically Zn^{2+} ion, one incompletely deprotonated H_2L^{2-} anion, one Bpp molecule and one crystal water molecule, as indicated in Fig. 1a. In

Table 2. Selected bond distances and angles for **I** and **II***

Bond	d, Å	Bond	d, Å
		I	
Zn(1)–O(2)	1.9187(12)	Zn(1)–N(2)$^{2\#}$	2.0443(15)
Zn(1)–O(4)$^{1\#}$	1.9374(12)	O(4)–Zn(1)$^{1\#}$	1.9375(12)
N(1)–Zn(1)	2.0349(15)	N(2)–Zn(1)$^{2\#}$	2.0443(15)
		II	
Ag(1)–N(1)$^{1\#}$	2.188(3)	Ag(1)–O(2)	2.323(2)
Ag(1)–N(2)	2.202(3)		
Angle	**ω, deg**	**Angle**	**ω, deg**
		I	
O(2)Zn(1)O(4)$^{1\#}$	116.61(5)	O(4)^{1}Zn(1)–N(1)	100.06(6)
O(2)Zn(1)N(1)	106.30(6)	O(4)^{1}Zn(1)–N(2)$^{2\#}$	107.23(6)
O(2)Zn(1)N(2)$^{2\#}$	122.87(6)	N(1)–Zn(1)–N(2)$^{2\#}$	99.80(6)
		II	
N(1)^{1}Ag(1)N(2)	131.22(10)	N(2)Ag(1)O(2)	111.11(9)
N(1)^{1}Ag(1)O(2)	117.63(9)		

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

this complex, the Zn^{2+} cation is located in a tetrahedral geometry [ZnN_2O_2] by two N atoms from two symmetry-related Bpp ligands, two oxygen atoms from two symmetry-related incompletely deprotonated H_2L^{2-} dianions. The Zn–O bond lengths are 1.9187(12) and 1.9374(12) Å for Zn(1)–O(2) and Zn(1)–O(4*B*). The Zn–N bond lengths are 2.0349(15) and 2.0443(15) Å for Zn(1)–N(1) and Zn(1)–N(2*A*).

Two adjacent [ZnN_2O_2] tetrahedral are connected together by a pair of H_2L^{2-} dianions adopting monodentate coordination mode to form a [$Zn_2(CO_2)_4N_4$] with the Zn···Zn distance of 5.0279(5) Å. The [$Zn_2(CO_2)_4N_4$] are extended by a couple of Bpp molecules to produce an infinite one-dimensional chain along a special direction (Fig. 1b). The structure of compound **I** extends into 3D supermolecular (Fig. 1d) array through two types of hydrogen bonds: (i) between coordination water molecules and carboxylate O atoms; (ii) between the two carboxyl O atoms of H_2L^{2-} ion. The detailed hydrogen bonds data are listed in Table 3. Besides, π–π interactions between two six-membered pyridine ring of Bpp ligands (centroid distance: 3.999 and 4.295 Å, Fig. 1c) further consolidate the stability of the resultant 3D network.

The asymmetric unit of **II** consists of one Ag^+ ion, one uncompletely deprotonated H_3L^- anion, one Bpp molecule and quarter crystal water molecule, as shown in Fig. 2a. In this complex, the Ag(I) is three-coordinated in a trigonal plane positioned at the center by two nitrogen atoms from two symmetry-related Bpp molecules and one oxygen atom from one H_3L^- anion. The bond lengths are 2.323(2) Å for Ag–O, 2.188(3) and 2.202(3) Å for Ag–N, respectively. The neighboring Ag(I) with the Ag–Ag separation of 14.113(6) Å were connected as a one-dimensional chain with the H_3L^- suspension arms by Bpp molecules (Fig. 2b). The adjacent chains are assembled into a 2D supramolecular layer (Fig. 2c) via two kinds of H-bondings interactions: (i) between the protonated carboxyl O atoms and unprotonated carboxyl O atoms; (ii) between the lattice water molecules and unprotonated carboxyl O atoms. The detailed hydrogen bonds data are listed in Table 3. Individual layers are cohered together to form its entire 3D supramolecular structure by stronger interlayer π–π interactions between two six-membered pyridine ring of Bpp ligands (centroid distance: 3.642 and 3.675 Å) as depicted in Fig. 2d. So, the H-bonding bonds and π–π interactions among the chains have great influence on the self-assembly and enhanced stability of the resultant structure.

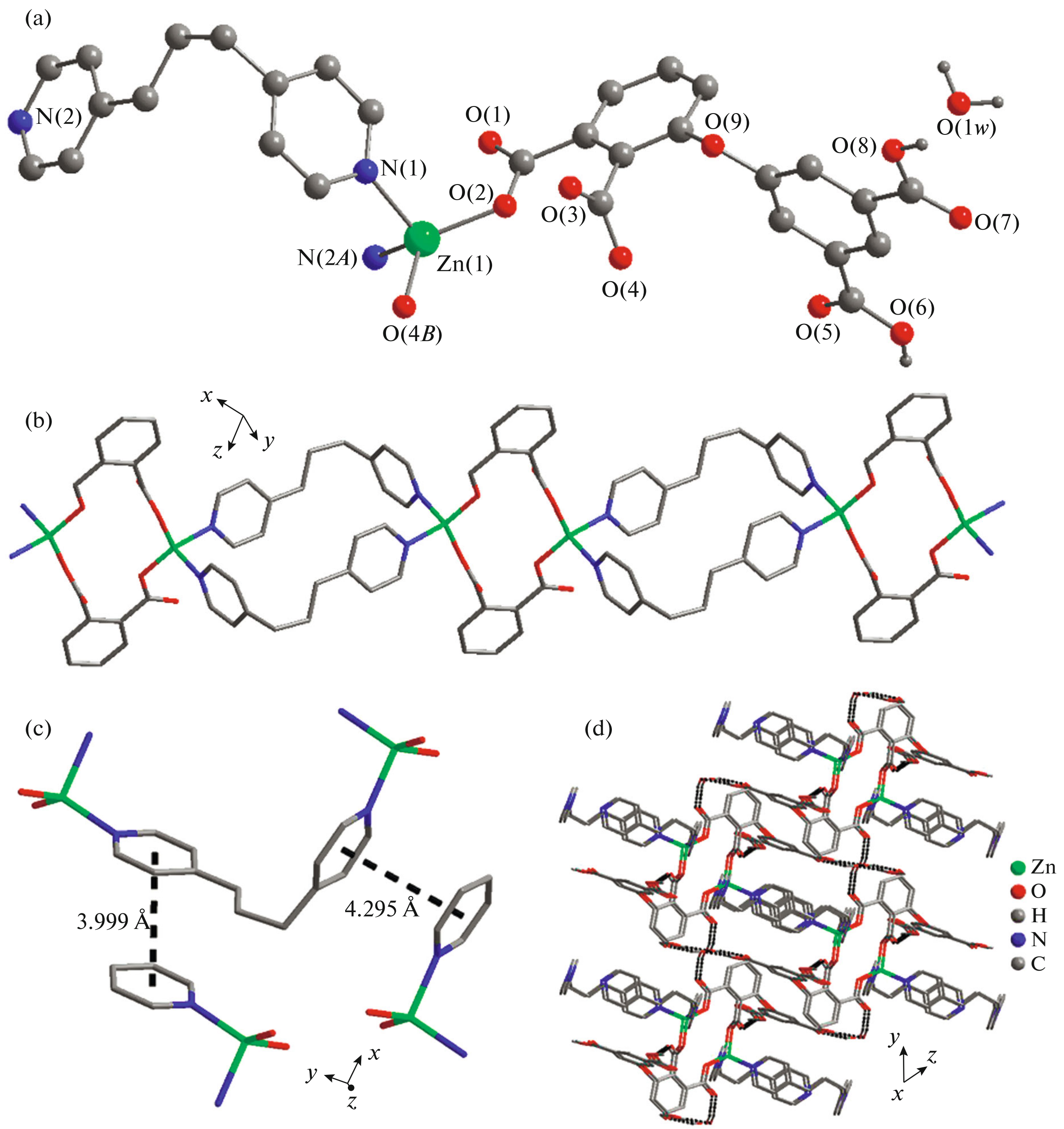

Fig. 1. Coordination environment of Zn(II) atoms in complex **I** (symmetry codes: $A = -x, 2 - y, -z$; $B = 1 - x, 1 - y, 1 - z$) (a); 1D chain of **I** (b); π–π interactions in **I** (c); 3D supramolecular architectures of **I** (d).

TG analyses of **I**, **II** were performed by heating the crystalline samples from room temperature to 700°C with a heating rate of 10°C min^{-1} under nitrogen atmosphere, as shown in Fig. 3. For **I**, an initial gradual weight loss (1.88%) from the room temperature to 173°C corresponds to the loss of one crystal water molecules (calcd. 2.88%). The framework of the complex **I** is stable up to ~276°C. Subsequently, the organic ligands decompose up till 470°C, the remaining 20.0% may be ZnO (calcd. 13.02%) and unburned carbon. For **II**, an initial not very obvious mass loss (0.70%) from room temperature to 193°C is in agreement with the removal of quarter solvent water molecule (calcd. 0.69%). Above 220°C, the framework begins to collapse owing to the decomposition of organic ligands, the final remnant 24.08% may be Ag_2O (calcd. 17.67%) and unburned carbon.

Complexes of d^{10} metal centers with nitrogen and caroxylate donor ligands are promisiong candidates for photoluminescent materials [21]. Coordination polymers have been reported to exhibit the ability to tune emission intensity of the free-organic ligands

Table 3. Geometric parameters of hydrogen bonds for **I** and **II***

D–H···A	Diatance, Å			Angle DHA, deg
	D–H	H···A	D···A	
I				
O(6)–H(6)...O(3)$^{1\#}$	0.82	1.84	2.6057(19)	154
O(8)–H(8)···O(1*w*)	0.82	1.83	2.590(2)	154
O(1*w*)–H(1*wA*)···O(7)$^{2\#}$	0.85	1.90	2.723(2)	161
O(1*w*)–H(1*wB*)···O(1)$^{3\#}$	0.85	1.93	2.750(2)	163
II				
O(3)–H(3)···O(1)$^{3\#}$	0.82	1.88	2.657(3)	158
O(6)–H(6)···O(2)$^{4\#}$	0.82	1.77	2.583(3)	174
O(8)–H(8)···O(1)$^{5\#}$	0.82	1.87	2.674(3)	165
O(10*w*)–H(1*w*)···O(7)$^{2\#}$	0.85	2.20	2.957(12)	149

* Symmetry codes: $^{1\#}$ $1 + x, y, z$; $^{2\#}$ $2 - x, -y, 3 - z$; $^{3\#}$ $1 - x, 1 - y, 2 - z$ (**I**); $^{2\#}$ $x, y - 1, z$; $^{3\#}$ $-x + 1/2, -y + 3/2, -z + 1$; $^{4\#}$ $-x + 1, -y + 2, -z + 1$; $^{5\#}$ $-x + 1/2, -y + 5/2, -z + 1$ (**II**).

after coordination with metals [22]. In this work, the solid-state luminescent properties of H_4L and compounds **I** and **II** have been investigated at room temperature and their emission spectra are given in Fig. 4. Emissions were observed at 417 nm ($\lambda_{ex} = 300$ nm) for the free H_4L ligand. It can be observed that intense emissions occur at 348 nm ($\lambda_{ex} = 310$ nm) for **I** and **II**. Thereinto, due to very weak fluorescent emission of the Bpp coligands, this emission can still be assigned to free H_4L ligand photoluminescence. Compared to the free H_4L ligand, the emission bands of **I** and **II** are 69 nm blue-shifted. And the blue-shift may be ascribed to the weak coujugation effects in comparison with those in the free ligand.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (no. 21571093), the Program for Science and Technology Innovation Talents

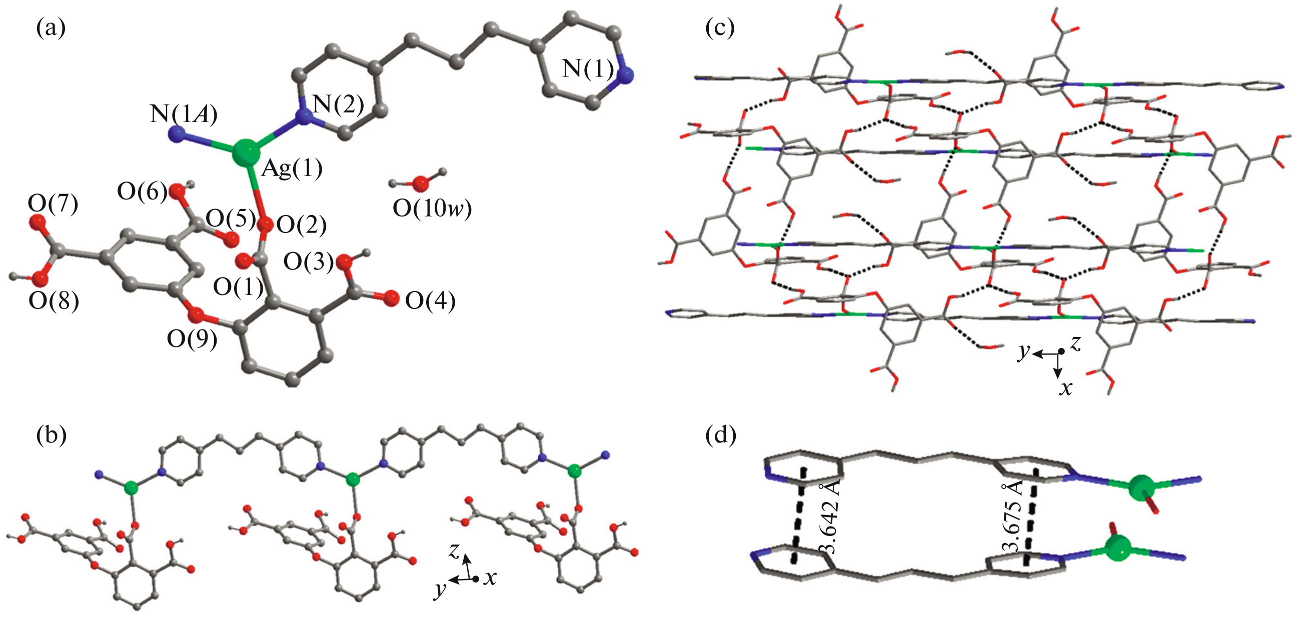

Fig. 2. Coordination environment of Ag(I) atoms in complex **II** (symmetry codes: *A* = *x*, 1 + *y*, *z*) (a); 1D chain of **II** (b); view of an H-bonding 2D layer (c); π–π interactions in **II** (d).

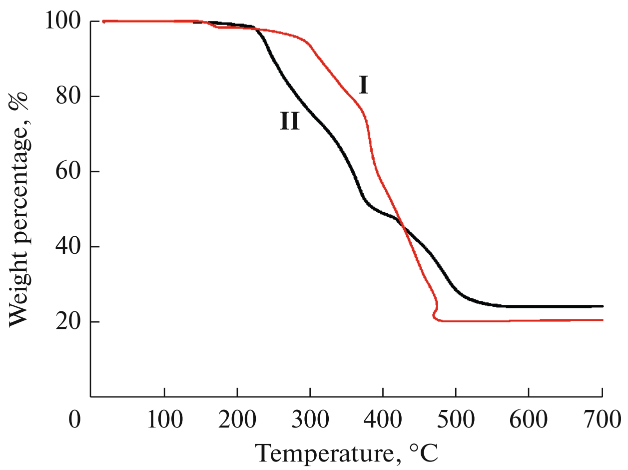

Fig. 3. The TGA curves for complexes **I** and **II**.

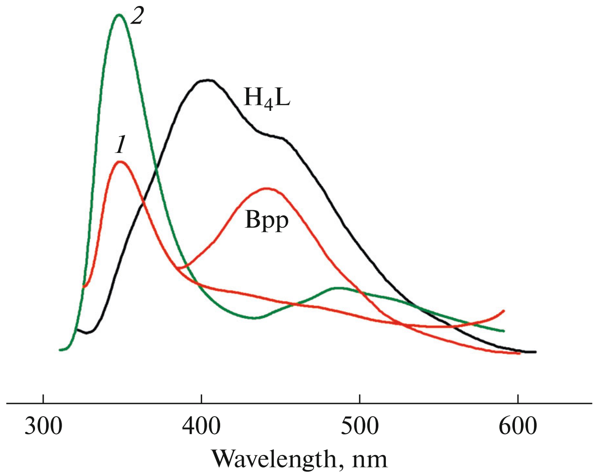

Fig. 4. The solid-state emission spectra of compounds **I**, **II** and the free H_4L and Bpp ligand at room temperature.

in Universities of Henan Province (no. 14HASTIT017), the Program for Innovative Research Team (in Science and Technology) in University of Henan Province (no. 14IRTSTHN008) and the Foundation of Science and Technology of Henan Province (nos. 162102210304 and 152102310348).

REFERENCES

1. Ren, H.Y., Yao, R.X., and Zhang, X.M., *Inorg. Chem.*, 2015, vol. 54, p. 6312.
2. Gangu, K.K., Maddila, S., Mukkamala, S.B., et al., *Inorg. Chim. Acta*, 2016, vol. 446, p. 61.
3. Hawes, C.S., Knowles, G.P., Chaffee, A.L., et al., *Cryst. Growth Des.*, 2015, vol. 15, p. 3417.
4. Sahu, J., Aijaz, A., Xu, Q., and Bharadwaj, P.K., *Inorg. Chim. Acta*, 2015, vol. 430, p. 193.
5. Manna, B., Chaudhari, A.K., Joarder, B., et al., *Angew. Chem. Int. Ed.*, 2013, vol. 52, p. 998.
6. Liu, G.Z., Li, X.D., Li, X.L., et al., *CrystEngComm*, 2013, vol. 15, p. 2428.
7. Wang, K.M., Du, L., Ma, Y.L., et al., *CrystEngComm*, 2016, vol. 18, p. 2690.
8. Plabst, M., McCusker, L.B., and Bein, T., *J. Am. Chem. Soc.*, 2009, vol. 131, p. 18112.
9. Cowan, M.G., Olguin, J., Narayanaswamy, S., et al., *J. Am. Chem. Soc.*, 2012, vol. 134, p. 2892.
10. Liu, G.Z., Li, X.L., Xin, L.Y., and Wang, L.Y., *CrystEngComm*, 2012, vol. 14, p. 5315.
11. Wang, K.M., Du, L., Ma, Y.L., et al., *CrystEngComm*, 2016, vol. 18, p. 2690.
12. Liu, D., Lu, K., Poon, C., and Lin, W., *Inorg. Chem.*, 2014, vol. 53, p. 1916.
13. Kitagawa, S. and Matsuda, R., *Coord. Chem. Rev.*, 2007, vol. 251, p. 2490.
14. Karmakar, A., Hazra, S., Silva, M.F.C.G.D., and Pombeiro, A.J.L., *New J. Chem.*, 2014, vol. 38, p. 4837.
15. Luo, X.L., Sun, L.B., Zhao, J., et al., *Cryst. Growth Des.*, 2015, vol. 15, p. 4901.
16. Wang, J.J., Hou, X.Y., Gao, L.J., et al., *Chin. J. Inorg. Chem.*, 2014, vol. 30, p. 1616.
17. Xantheas, S., *Chem. Phys.*, 2000, vol. 258, p. 225.
18. Ma, L.F., Wang, L.Y., Wang, Y.Y., et al., *Inorg. Chem.*, 2009, vol. 48, p. 915.
19. Sheldrick, G.M., *SHELXS-97, Program for the Solution of Crystal Structures*, Göttingen, Univ. of Göttingen, 1997.
20. Sheldrick, G.M., *SHELXL-97, Program for the Refinement of Crystal Structures*, Göttingen, Univ. of Göttingen, 1997.
21. Allendorf, M., Bauer, C., Bhakta, R., and Houk, R., *Chem. Soc. Rev.*, 2009, vol. 38, p. 1330.
22. Huang, H.Q., Wang, D.F., Zhang, T., and Huang, R.B., *J. Mol. Struct.*, 2015, vol. 1086, p. 99.