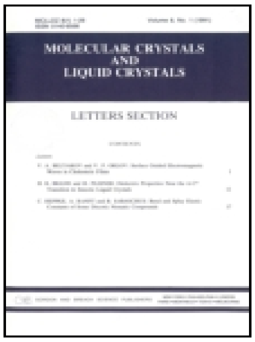

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A Novel Cu(II) Coordination Polymer Containing Single-stranded Helical Chains: Crystal Structure, Thermal Stability, and Fluorescent Property

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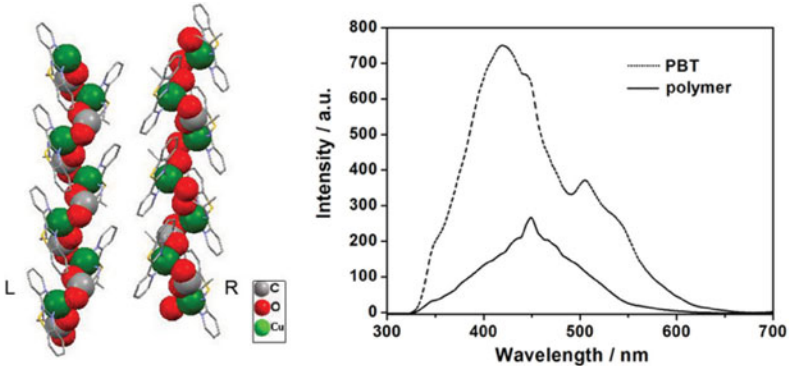
Graphic Abstract:



The reaction of 2-(2′-pyridyl)benzothiazole, L-alanine and perchlorate copper salt in methanol/water system affords a novel Cu(II) coordination polymer [Cu(PBT)(L-Ala)]$_n$(ClO$_4$)$_n$ [PBT = 2- (2′- pyridyl)benzothiazole, L-Ala = L-alaninate]. The structure of the polymer has been determined by elemental analysis, IR, X-ray single-crystal diffraction. The results reveal the carboxyl oxygen atoms of L-Ala brige adjacent Cu(II) atoms into 1D single-stranded chiral helical chains, and the Cu(II) coordination polymer consists of the left- and right-hand helical chains arranging alternately. In the Cu(II) coordination polymer, there exist strong aromatic π–π stacking interactions between benzothiazole rings and pyridyl rings, and hydrogen bonding interactions between perchlorate groups and the helical trains. Moreover, the thermal stability and fluorescent properties of the polymer are described.

Keywords Cu(II) coordination polymer; fluorescent property; helical structure; thermal stability

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Over the past decades, helical coordination polymers have drawn extensive attention due to their intriguing topologies, as well as their potential application in asymmetric catalysis, second-order nonlinear optics, magnetic materials, and enantioselective separations [1–3]. Studies on the synthesis about helical coordination polymers are of continued interest, while search for methodology on the rational design and synthesis of the desired coordination polymers still remains a long-term challenge in coordination chemistry and supermolecule chemistry. Many factors can affect the self-assembly process of coordination polymers, including geometric requirement of metal ions, the solvent system, building-block ligands, temperature, pH value, counterions, etc. [4–6]. In particular, building-block ligands play vital roles in the self-assembly process.

The flexible asymmetric bridging ligands are one of important building-block ligands to construct helical coordination polymers [7]. Among them amino acids have been demonstrated as the top-rank candidates owing to their natural occurrence (L-α-amino acids), multiple metal binding sites, and versatile bonding modes provided by the carboxylate groups [8]. Importantly, the presence of amino acids is beneficial to formation of the intrinsic chirality of helical chains, which is the most feature of helical chains in helical coordination polymers. Up to now, many helical coordination polymers containing amino acids have been reported [7–14]. In addition, rigid *N*-heterocyclic rings compounds containing pyridine, imidazole, and thiazole moiety also have been widely employed to construct helical coordination polymers [15–19]. However, helical coordination polymers based on 2-(2′-pyridyl)benzothiazole (PBT) and L-α-amino acids ligands, to our best known, have not been founded to date. In this paper, we describe the synthesis, crystal structure, thermal stability, and fluorescent property of a novel Cu(II) helical coordination polymer $[\mathrm{Cu(PBT)}(L\text{-Ala})]_n(\mathrm{ClO_4})_n$.

Experimental

Materials and Physical Measurements

2-(2′-pyridyl)benzothiazole (PBT) was prepared according to the literature [20]. Other reagents and solvents were received commercially available, and employed without further purification. Water is deionized water.

Elemental analyses were carried out by a Vario EL elemental analyzer. The infrared spectrum was performed with a Nicolet ACATAR 360 FT-IR spectrometer in the range of $4000 \sim 400\ \mathrm{cm^{-1}}$ (KBr discs). The crystal structure was determined by Smart 1000 CCD single crystal X-ray diffractometer. The thermostability was monitored in an N_2 atmosphere with a heating rate of $10^\circ\mathrm{C\ min^{-1}}$ on DTG-60 Simultaneous Thermogravimetry/Differential Thermal Analyzers. Fluorescence spectra were recorded on an RF-5301 spectrophotometer equipped with 1.0 cm quartz cells.

Synthesis of the Cu(II) Coordination Polymer

To a methanol solution (20 mL) of PBT (0.106 g, 0.5 mmol) and $\mathrm{Cu(ClO_4)_2}$ (1 mL 0.5 mol $\mathrm{L^{-1}}$) was added slowly an aqueous solution (5 mL) of deprotonated L-Ala (0.0445 g, 0.5 mmol). The reaction mixture was stirred for 2 h in air at 60°C, and then cooled to room temperature, and its pH value was adjusted to 5.5. The resultant solution was left for slow evaporation at room temperature. After several weeks, green crystals suitable for X-ray structure determination were collected in 70% yield. IR (KBr, cm^{-1}): 3301, 3259, 1615, 1558, 1498, 1462, 1419, 1093, 766, 619. Anal. Calcd for C_{15} H_{14} Cu N_3 O_2 S Cl O_4: C 38.88; H 3.05; N 9.07. Found: C 38.69; H 3.12; N 8.74%.

X-ray Crystallographic Determination

The crystallography data for the Cu(II) coordination polymer were collected at 173 K on a Bruker Smart 1000 CCD system diffractometer using graphite monochromatic Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were obtained with least squares refinements, and semiempirical absorption corrections were applied to the diffraction data for the structure. The structure was solved by direct methods and difference Fourier syntheses [21], and was refined on F^2 by the full-matrix least-squares techniques using SHELXL-97 package [22]. Hydrogen atoms were introduced at calculated positions as riding on bonded atoms, and all non-hydrogen atoms were refined anisotropically. Crystal and structure refinement data for the polymer were given in Table 1.

Results and Discussion

IR Spectra

IR spectrum of the Cu(II) coordination polymer shows a strong absorption band centered near 1498 cm^{-1}, which is mostly attributed to $\nu_{C=N}$ of the thiazolyl ring. The band is shifted about 10 cm^{-1} toward lower wavelength number compared to that of free ligand PBT, suggesting nitrogen atoms of PBT coordinate to the central Cu(II) ion. The bands at 1615 cm^{-1} and 1462 cm^{-1} can be assigned to the skeletal vibration of benzene ring. Two sharp signals at 3301 cm^{-1} and 3259 cm^{-1} correspond to the asymmetric and symmetric N—H stretching frequencies of the amino group, respectively. Moreover, the absence of any band in the region of 1750 to 1700 cm^{-1} in the IR spectrum of the isolated polymer demonstrates the carboxyl group of *L*-Ala coordinating to the central Cu(II) ion. Accordingly, the strong bands at 1558 cm^{-1} and 1419 cm^{-1} are assigned to the asymmetric and symmetric stretching modes of the carboxylate group, respectively. The difference value between them is 139 cm^{-1}, indicating the carboxylate group serves as a bridging group [23], which is consistent with the result obtained by the single crystal X-ray diffraction. In addition, the medium bands of ν_{Cu-N} and ν_{Cu-O} were observed at 766 and 619 cm^{-1}, respectively. The strong band at 1093 cm^{-1} is characteristic of ν_{Cl-O} of perchlorate group.

Crystal Structure of the Cu(II) Coordination Polymer

ORTEP diagram depicting the coordination sphere for the polymer [Cu(PBT)(*L*-Ala)]$_n$(ClO$_4$)$_n$ is given in Fig. 1. The main bond lengths and bond angles are listed in Table 2. The polymer crystallizes in a monoclinic system with $P2_1$ space group, and extends as 1D helical chains supplemented by extensive intramolecular hydrogen bonding and aromatic stacking interactions. As shown in Fig. 1, there are two crystallographically independent [Cu(PBT)(*L*-Ala)](ClO$_4$) molecules in the unit cell. Each Cu(II) metal center possess a distorted *tetragonal pyramid* with N_3O_2 coordination sphere, in which Cu1 is coordinated by two N atoms (N1 and N2) of the ligand PBT and one N atom and O atom(N3 and O1) of *L*-Ala, while Cu2 is coordinated by N4, N5 of PBT and N6, O2 of *L*-Ala, O3

Table 1. The crystal data and structure refinement parameters for the Cu(II) coordination polymer

Identification code	The polymer
Empirical formula	C_{15} H_{14} Cu N_3 O_2 S Cl O_4
Formula weight	463.34
Temperature (K)	173
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	11.019(2)
b (Å)	7.7788(15)
c (Å)	20.389(4)
A (°)	90
β (°)	97.534(3)
γ (°)	90
V (Å^3)	1732.6(6)
Z	4
D_c (g cm^{-3})	1.776
$F(000)$	940
Crystal size (mm^3)	0.16 × 0.39 × 0.43
Mu(MoKa) (mm)	1.576
Wavelength (Å)	0.71073
θ range (°)	1.9–27.0
Index ranges	$-4 \leq h \leq 14$, $-9 \leq k \leq 9$, $-25 \leq l \leq 24$
Reflections collected	8747
Independent reflections	7004 ($R_{int} = 0.016$)
Observed data ($I > 2\,\sigma(I)$)	5680
Data/restraints/parameters	7004/1/489
Flack x	0.019(17)
Final R indices ($I > 2\,\sigma(I)$)	$R^1 = 0.0350$, $wR^2 = 0.0875$
R indices (all data)	$R^1 = 0.0474$, $wR^2 = 0.0939$
$\Delta\rho_{max}$, $\Delta\,\rho_{min}$ (e Å^{-3})	0.885, −0.324

and O4 of the carboxylate groups at the apical position brige Cu1 and Cu2 to form 1D chiral helical chains, respectively. Thus, for **Cu1** and **Cu2** molecules, two five-member rings are formed between the central Cu and the ligands PBT and *L*-Ala, respectively. Accordingly, the dihedral angle of two five-member rings of **Cu1** cation is 117.6°, and that of **Cu2** cation is 78.2°. In addition, N1, N2, O1, and Cu1 atoms for **Cu1** plane deviate by 0.0311, −0.0010, 0.0316, and −0.0617 Å, respectively, from the least-squares plane $0.2271\,x + 0.3962\,y + 0.8896\,z = -15.1372$ defined by the four ligating atoms, suggesting the four equatorial atoms in the cation are nearly coplanar. Another basal plane atom N3 occupies the distortion position, and the distance from N3 to **Cu1** plane is 1.7127 Å, whereas the distance of the axial atom O3 to **Cu1** plane is 20062 Å. The Cu1–N bonding lengths range from 1.997(4) to 2.211(5) Å, and the bond length of Cu1–O3 (2.005(3) Å) is larger than that of Cu1–O1(1.963(4) Å), which are similar to the cases of amino acidato complexes reported earlier [8, 13, 14]. Similarly, for the **Cu2** plane, N4, N5, O2, and Cu2 atoms derivate

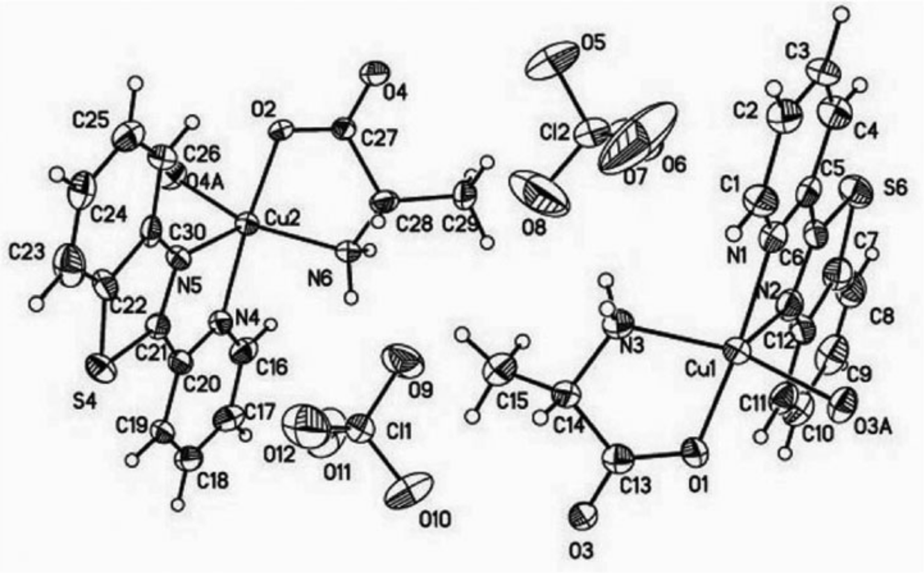

Figure 1. ORTEP diagram of the Cu(II) coordination polymer.

Table 2. The main bond lengths [Å] and bond angles [deg (°)] for the Cu(II) coordination polymer, Symmetry code for the polymer *a*: $1 - x$, $1/2 + y$, $1 - z$

	Distances		
Cu1–N1	2.008(4)	Cu2–N5	2.219(4)
Cu1–N2	2.211(5)	Cu2–N6	1.988(4)
Cu1–N3	1.997(4)	Cu2–O2	1.965(4)
Cu1–O3	2.005(3)	Cu2–N4	2.018(4)
Cu1–O1	1.963(4)	Cu2–O4^a	1.986(3)
N1–C1	1.344(8)	N5–C30	1.377(7)
N1–C5	1.347(7)	N5–C21	1.309(6)
N2–C6	1.290(7)	N4–C20	1.353(6)
N2–C12	1.406(7)	N4–C16	1.320(7)
	Angles		
O3–Cu1–N1	92.81(16)	O2–Cu2–N4	174.08(14)
O3–Cu1–N2	95.48(15)	O2–Cu2–N5	99.76(15)
O3–Cu1–N3	148.79(16)	O2–Cu2–N6	83.05(15)
O1–Cu1–O3	92.70(15)	O2–Cu2–O4^a	89.12(14)
O1–Cu1–N1	174.26(16)	N4–Cu2–N5	79.24(16)
O1–Cu1–N2	98.55(16)	N4–Cu2–N6	91.82(16)
O1–Cu1–N3	83.61(16)	O4^a–Cu2–N4	96.79(15)
N1–Cu1–N2	79.29(17)	N5–Cu2–N6	110.60(15)
N1–Cu1–N3	92.51(17)	O4^a–Cu2–N5	96.78(14)
N2–Cu1–N3	115.72(17)	O4^a–Cu2–N6	152.40(15)

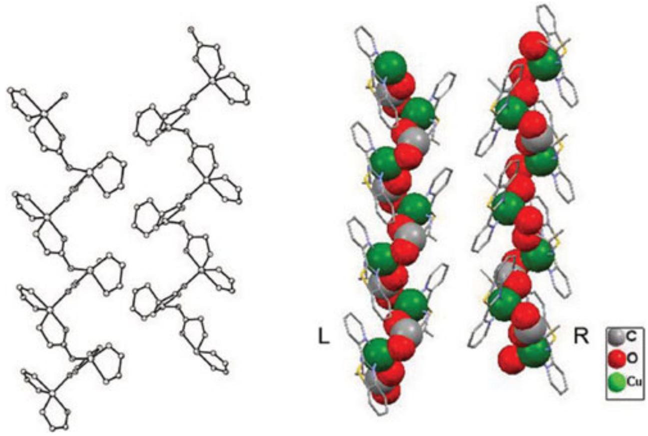

Figure 2. Chiral single-stranded helical chains of the Cu(II) coordination polymer.

by −0.0336, 0.0004, −0.0345, and 0.0677 Å, respectively, from the least-squares plane $0.2239\,x + 0.3965\,y + 0.8903\,z = -4.8819$ defined by the four ligating atoms, indicating the four equatorial atoms in the cation are nearly coplanar. Another basal plane atom N6 occupies the distortion position, and the distance from N6 to **Cu2** plane is 1.7713 Å, while the distance of the axial atom O4 to **Cu2** plane is 2.0434 Å. The Cu2–N bonding lengths range from 1.988(4) to 2.219(4) Å, and the bond length of Cu2–O4 (1.986 Å) is slightly larger than that of Cu2–O2 (1.965 Å).

The noteworthy feature of this polymer is that the oxygen atoms of the carboxylate group brige each pair of adjacent Cu(II) atoms into chiral helical chains with a long pitch of 7.779 Å, in which two monomers serve as a cycle, and the distance of Cu ··· Cu is 4.995 Å. As the chirality of *L*-Ala can affect the whole helical chains, the left- and right-hand single-stranded helical chains are formed with benzothiazole rings decorating at the two sides of the long chains, respectively. Moreover, these benzothiazole rings at each side of the helix are arranged in a parallel fasion (Fig. 2). The polymer consists of 1D left- and right-hand single-stranded helical chains arranging alternately, which is similar with the structure of the coordiantion polymers reported in the literatures [24, 25]. In addition, may be 2-(2′-pyridyl)benzothiazole is rigid plane ligand and absent in the flexibility, these left-hand and right-hand single-strand helical trains cannot further form the double- or multi-stranded trains [26].

π—π stacking interactions between the benzothiazole rings and pyridyl rings on each side of the helical chains play a vital role in enhancing the stability of Cu(II) coordination polymer. The centroids distance of benzothiazole and pyridyl rings is 3.538 Å, indicating that there is a strong aromatic π—π stacking interaction between the two rings [27,28] (Fig. 3). Additionally, plenty of intermolecular hydrogen bonds, N—H ··· O and C—N ··· O, are formed between perchlorate groups and the helical trains (Fig. 4), while there is scarcely intramolecular hydrogen bonds in each helical chain except for C4—H4 ··· S6 (C4 ··· S6 = 3.179(7) Å) and C19—H19 ··· S4 (C19 ··· S4 = 3.187(6) Å). By these complicated hydrogen bonds interactions, adjacent helical trains are connected to further promote the stability of the whole coordination polymer. The data of intra- and intermolecular hydrogen bonds are given in Table 3.

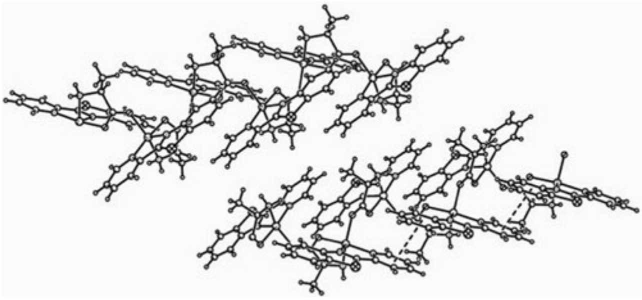

Figure 3. π–π stacking interactions between benzothiazole and benzene rings.

Thermostability of the Cu(II) Coordination Polymer

Thermogravimetric experiment was conducted to study the thermal stability of the Cu(II) coordination polymer, which is an important parameter of metal–organic coordination polymers. The TG curve of the polymer was recorded in the temperature range of room temperature to 800°C. As shown in Fig. 5, the polymer is thermally stable up to 190°C, and on further heating it lost perchlorate groups and became the intermediate species $[Cu(PBT)(L\text{-}Ala)]_n^+$ until 221°C (process a: weight loss, observed: 21.8, calculated: 21.5%), which lost the ligand 2-(2′-pyridyl)benzothiazole in the temperature range of 223–371°C (process b: weight loss, observed: 44.6, calculated: 45.8%). The last observed weight loss corresponds

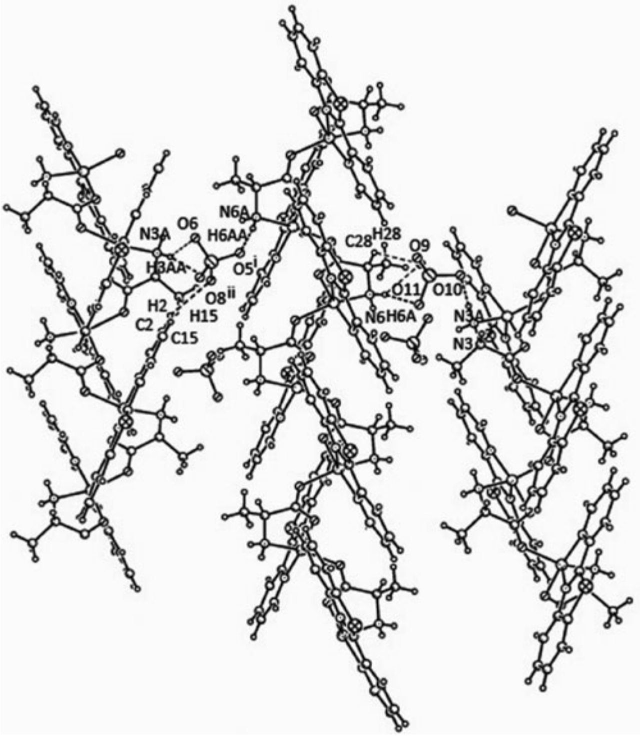

Figure 4. Intermolecular hydrogen bond interactions.

Table 3. Intra- and intermolecular hydrogen bonds of the Cu(II) coordination polymer, Symmetry codes for the polymer b: x, $-1+y$, z; c: x, $1+y$, z; d: $-1+x$, $-1+y$, $-$; e: $1+x$, $1+y$, z

D–H $\cdots$ A	D–H (nm)	H $\cdots$ A (nm)	D $\cdots$ A (nm)	$\angle$ D–H $\cdots$ A (°)
N3–H3A $\cdots$ O10^b	0.09200	0.22300	0.3095(7)	156.00
N3–H3B $\cdots$ O6	0.09200	0.25100	0.3308(9)	145.00
N3–H3B $\cdots$ O8	0.09200	0.25900	0.3480(7)	163.00
N6–H6A $\cdots$ O9	0.09200	0.23100	0.3055(5)	138.00
N6–H6A $\cdots$ O11	0.09200	0.26000	0.3494(6)	164.00
N6–H6B $\cdots$ O5^c	0.09200	0.22000	0.3113(6)	173.00
C2–H2 $\cdots$ O8^b	0.09500	0.25800	0.3446(8)	152.00
C3–H3 $\cdots$ O7^b	0.09500	0.25300	0.3222(9)	130.00
C4–H4 $\cdots$ O12^d	0.09500	0.24700	0.3333(7)	152.00
C15–H15C $\cdots$ O8	0.09800	0.25700	0.3243(7)	126.00
C19–H19 $\cdots$ O7^e	0.09500	0.25200	0.3327(7)	142.00
C28–H28 $\cdots$ O9	0.10000	0.25600	0.3140(5)	117.00

to the release of *L*-Ala in the range of 383–765 °C (process c: observed: 19.2, calculated: 19.2%). The residues are copper(II) oxide.

The Fluorescent Property for the Cu(II) Coordination Polymer

The copper coordination polymers have been investigated for fluorescent property and for potential applications as functional solid materials [29]. In this work, the fluorescent properties of the title polymer as well as the PBT ligand in the solid state were investigated in the wavelength range of 280–800 nm at room temperature (Fig. 6). As seen, the ligand PBT shows multiple emission peaks at 348, 420, 445, and 505 nm ($\lambda_{ex} = 279$ nm). However, the

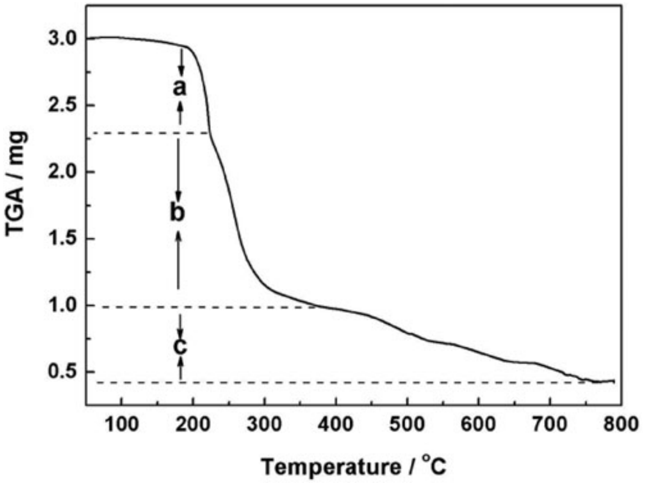

Figure 5. Thermal degradation curve of the Cu(II) coordination polymer.

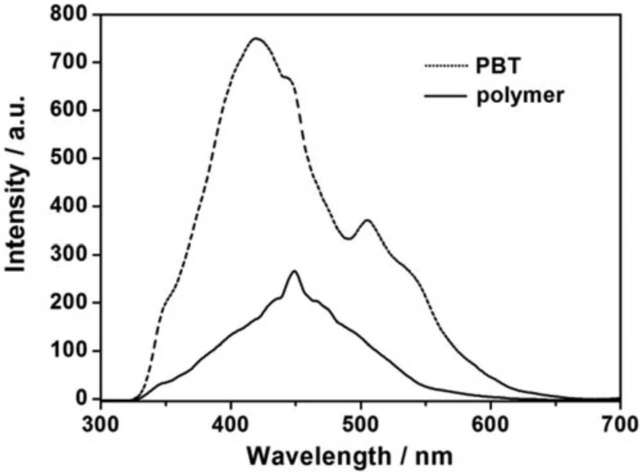

Figure 6. The emission spectra of PBT (dash) and the Cu(II) coordination polymer (solid).

polymer exhibits a weak emission at 347 nm and a strong emission at 450 nm ($\lambda_{ex} = 279$ nm) with a shoulder peak at 471 nm in the wavelength range of 400–500 nm. Furthermore, in comparison with PBT, the emission maximum of the polymer has a redshift of 30 nm, which is indicative of metal-to-ligand (MLCT) charge transition, suggesting the coordination of large π-system ligand PBT to Cu leading to the increase of PBT conformational rigidity and the decrease of the overall energy of the system [30, 31]. Meantime, the peak at 347 nm in the emission spectrum for the polymer can be attributed to intraligand ($\pi \rightarrow \pi^*$) charge transfer [32, 33].

Conclusions

In summary, a novel Cu(II) helical coordination polymer $[\mathrm{Cu(PBT)}(L\text{-Ala})]_n(\mathrm{ClO_4})_n$ has been synthesized and characterized by elemental analysis, IR, X-ray single-crystal diffraction analysis, TG technique and fluorescence spectrum. Each Cu(II) metal center possess a distorted tetragonal pyramid with an N_3O_2 coordination sphere in which PBT is coordinated by two nitrogen atoms to form a five number chelated ring, and the deprotonated *L*-Ala is coordinated through one amino nitrogen atom and one carboxylate oxygen atom to form a five number chelated ring with another carboxylate oxygen atom of *L*-Ala briging adjacent Cu(II) atoms into a helical chain. The Cu(II) polymer consists of 1D left- and right-hand helical chains arranging alternately. In the polymer, there exist strong aromatic π–π stacking interactions between benzothiazole rings and pyridyl rings, and hydrogen bonding interactions between perchlorate groups and the helical trains. Thermogravimetric experiment exhibits the polymer has good thermal stability. The fluorescence spectrum of the Cu(II) coordination polymer shows the two main emission peaks at 347 nm and 450 nm. The results further enrich the crystallographic and fluorescent database of Cu(II) helical coordination polymers.

Acknowledgments

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this paper have been deposited in the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge, CB2 1EZ, UK) as supplementary publications No.CCDC-905039 for $[Cu(PBT)(L\text{-}Ala)]_n(ClO_4)_n$ and are available on request quoting.

References

[1] Kirillov, A. M., Kirillova, M. V., & Pombeiro, A. J. L. (2012). *Coord. Chem. Rev.*, *256*, 2741.
[2] Yin, Y. Y., Cao, X. C., Cheng, P., & Ma, J. G. (2012). *Inorg. Chem. Commun.*, *24*, 7.
[3] Wang, X. F., Li, L., Kong, Y. M., & Liu, Y. (2012). *Inorg. Chem. Commun.*, *21*, 72.
[4] Li, G. B., He, J. R., Liu, J. M., & Su, C. Y. (2012). *Cryst. Eng. Commun.*, *14*, 2152.
[5] Ren, C., Liu, P., Wang, Y. Y., Huang, W. H., & Shi, Q. Z.(2010). *Eur. J. Inorg. Chem.*, *2010*, 5545.
[6] McMorran, D. A.(2008). *Inorg. Chem.*, *47*, 592.
[7] Han, L., & Hong, M. C. (2005). *Inorg. Chem. Commun.*, *8*, 406.
[8] Kathalikkattil, A. C., Bisht, K. K., Aliaga-Alcalde, N., & Suresh, E. (2011). *Cryt.Growth Des.*, *11*, 1631.
[9] Dong, L. J., Chu, W., Zhu, Q. L., & Huang, R. D.(2011). *Cryst. Growth Des.*, *11*, 93.
[10] Vaidhyanathan, R., Bradshaw, D., Rebilly, J. N., Barrio, J. P., Gould, J. A., Berry, N. G., & Rosseinsky, M. J. (2006). *Angew. Chem., Int. Ed.*, *45*, 6495.
[11] Xiao, D. R., Zhang, G. J., Liu, J. L., Fan, L. L., Yuan, R., & Tong, M. L. (2011). *Dalton Trans.*, *40*, 5680.
[12] Ingleson, M. J., Barrio, J. P., Bacsa, J., Dickinson, C., Park, H., & Rosseinsky, M. J. (2008). *Chem. Commun., 11*, 1287.
[13] Maclaren, J. K., & Janiak, C.(2012). *Inorg. Chim. Acta*, *389*, 183.
[14] Ohmura, S. D., Moriuchi, T., & Hirao, T. (2013). *J. Inorg. Organomet. Polym.*, *23*, 251.
[15] Albrecht, M. (2001). *Chem. Rev.*, *101*, 3457.
[16] Lu, W. G., Gu, J. Z., Jiang, L., Tan, M. Y., & Lu, T. B.(2008). *Cryst. Growth Design*, *8*, 192.
[17] Zhang, Sh., Cao, Y. N., Zhang, H. H., Chai, X. C., & Chen, Y. P. (2008). *J. Solid State Chem.*, *181*, 399.
[18] Geng, X. H. Feng, Y. L., & Lan, Y. Z. (2009). *Inorg. Chem. Commun.*, *12*, 447.
[19] Lu, J., Yin, H. D., Liu, H. T., Wang, S. N., Li, D. C., & Dou, J. M. (2012). *Inorg. Chem. Commun.*, *26*, 7.
[20] Kumar, D., Rudrawar, S., & Chakrabor, A. K. (2008). *Aust. J. Chem.*, *61*, 881.
[21] Sheldrick, G. M. (1997). *SHELXS-97: Structure Solving Program*, University of Göttingen: Germany.
[22] Sheldrick, G. M. (1997). *SHELXL-97: Crystal Structure Refinement Program*, University of Göttingen: Germany.
[23] Nakamoto, K. (2009). *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry (6th Edition)*, Chapter 1, John Wiley and Sons. Inc.: New York, 65.
[24] Lu, W. G., Gu, J. Z., Jiang, L., Tan, M. Y., & Lu, T. B. (2008). *Cryst. Growth Des.*, *8*, 192.
[25] Feng, X., Liu, L., Zhou, J. G., Zhou, L. L., Shi, Z. Q., & Wang, L. Y. (2013). *Synth. React. Inorg. M.*, *43*, 705.
[26] Chen, X. M., & Liu, G. F. (2002). *J. Chem. Eur.*, *8*, 4811.
[27] Hunter, C. A., & Sanders, J. K. (1990). *J. Am. Chem. Soc.*, *112*, 5525.
[28] Tong, M. L., Chen, H. J., & Chen, X. M. (2000). *Inorg. Chem.*, *39*, 2235.
[29] Peng, R., Li, M., & Li, D. (2010). *Coord. Chem. Rev.*, *254*, 1.
[30] Ni, J., Wei, K. J., Min, Y. Z., Chen, Y. W., Zhan, S. Z., Li, D., & Liu, Y. Z. (2012). *Dalton Trans.*, *41*, 5280.
[31] Chen, H. F., Yang, W. B., Lin, L., Guo, X. G., Dui, X. J., Wu, X. Y., Lu, C. Z., & Zhang, C. J. (2013). *J. Solid State Chem.*, *201*, 215.
[32] Fan, Y. H., Wang, J. L., Bai, Y., Dang, D. B., & Zhao, Y. Q. (2012). *Synth. Met.*, *162*, 1126.
[33] Bai, Yan., Gao, H., Qi, Z. Y., & Dang, D. B. (2012). *Synth. React. Inorg. M.*, *42*, 53.