

## 4-氯苯乙酸构筑的一维铅配位聚合物的晶体结构、 荧光性质和生物活性

薛俭雷 田春华\*

(齐齐哈尔医学院医学技术学院, 齐齐哈尔 161006)

**摘要:** 水热条件下采用  $\text{Pb}(\text{NO}_3)_2$  和 4-氯苯乙酸作为反应物合成出 1 个新的一维铅配位聚合物  $[\text{Pb}(\text{4-cpa})_2(\text{H}_2\text{O})]_n$  (**1**) (4-Hcpa=4-氯苯乙酸), 并分别用元素分析、红外光谱、差热分析、X-射线粉末衍射和 X-射线单晶衍射等表征了该结构。晶体结构分析结果表明:  $\mu_3$  桥联的 4-氯苯甲酸将铅金属离子连接成一维链结构。荧光分析表明常温固态下配合物 **1** 发射蓝色荧光, 且在 422 nm 处的荧光寿命为 5.3 ns。以除草剂-精喹禾灵为对照品, 考察了配体 4-Hcpa 和配合物 **1** 的生物活性。

**关键词:** 铅配位聚合物; 水热合成; 晶体结构; 荧光性质; 生物活性

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## Lead(II) Coordination Polymer with 4-Chlorophenoxyacetate as Ligand: Structure, Luminescence and Biological Activity

XUE Jian-Lei TIAN Chun-Hua\*

(Medical Technology Department, Qiqihar University, Qiqihar, Heilongjiang 161006, China)

**Abstract:** A new 1D lead(II) coordination polymer,  $[\text{Pb}(\text{4-cpa})_2(\text{H}_2\text{O})]_n$  (**1**, 4-cpa=4-chlorophenylacetate), has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectroscopy, TGA, powder X-ray diffraction and single crystal X-ray diffraction. Structural determination reveals that **1** exhibits an interesting 1D chain structure constructed by 4-cpa ligands. Solid-state **1** emits the intensely blue photoluminescence with fluorescence lifetime of 5.3 ns (422 nm) at room temperature. The 4-Hcpa ligand and complex **1** have been screened for their phyto-growth-inhibitory activities against *Brassica napus* L. and *Echinochloa crusgalli* L., and the results are compared with the activity of quizalofop-*p*-ethyl. CCDC: 946824.

**Key words:** lead(II) coordination polymer; hydrothermal synthesis, crystal structure, luminescence, biological activity

In recently years, coordination complexes have attracted considerable interest due to their intriguing architectures, topologies, and applications in areas such as catalysis, separation, sorption, luminescence, magnetism, and biological chemistry<sup>[1-6]</sup>. Construction of coordination polymers depends on metal ions, organic ligands, solvent system, synthetic methods,

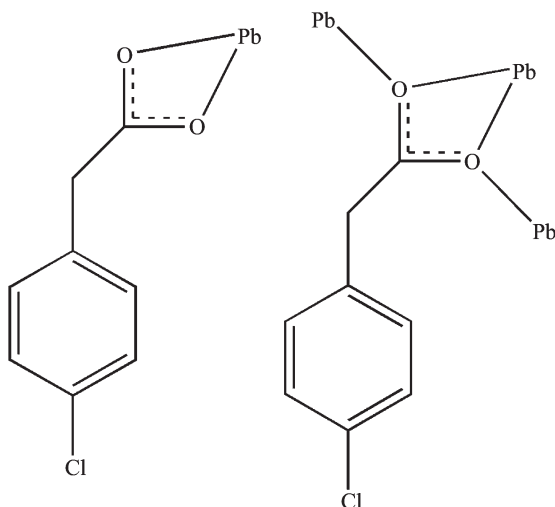
pH, reaction temperature<sup>[7]</sup>, especially selection and utilization of building blocks. Fascinating coordination polymers have been constructed by carboxylate ligands because of their ability to possess unusual structures and their sensitivity to molecular environments<sup>[8]</sup>. The anion of the 4-chlorophenylacetate (4-cpa) molecule possesses one carboxylate group, which

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\*通讯联系人。E-mail: tianchunhua1980@163.com; Tel: 0452-2663153

might be utilized as a versatile linker for constructing interesting coordination polymers. However, so far, work on the construction of metals coordination polymers based on 4-Hcpa ligand is still very scarce<sup>[9]</sup>. On the basis of above considerations, we chose 4-chlorophenylacetic acid (4-Hcpa) as the single ligand to construct the title 1D lead coordination polymer,  $[\text{Pb}(\text{4-cpa})_2(\text{H}_2\text{O})]_n$  (**1**), under hydrothermal conditions. Structural characterization and photoluminescent properties of **1** are reported here. Moreover, the biological activities of 4-Hcpa and **1** are also investigation.



Scheme 1 Coordination modes of 4-cpa ligands in the structure of **1**

## 1 Experimental

### 1.1 Materials and measurements

All chemicals were commercially available and used as received without further purification. Elemental analyses for C, H, and N were carried out by using a Vario EL III Elemental Analyzer. Infrared spectra were recorded (4 000~400  $\text{cm}^{-1}$ ) as KBr disks on a Shimadzu IR-440 spectrometer. Powder XRD investigations were carried out on a Bruker AXS D8-Advanced diffractometer at 40 kV and 40 mA with  $\text{Cu K}\alpha$  ( $\lambda=0.154\,06\text{ nm}$ ) radiation. Luminescence spectra and lifetime for crystal solid samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter. Thermogravimetry analyses (TGA) were performed on an automatic simultaneous thermal analyzer (DTG-60, Shimadzu) under a flow of  $\text{N}_2$  at a

heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  between ambient temperature and  $800\text{ }^\circ\text{C}$ .

### 1.2 Synthesis of complex **1**

A mixture of  $\text{Pb}(\text{NO}_3)_2$  (0.166 g, 0.5 mmol), 4-Hcpa (0.085 g, 0.5 mmol), NaOH (0.01 g, 0.25 mmol) and  $\text{H}_2\text{O}$  (15 mL) was sealed in a 23 mL Teflon reactor and kept under autogenous pressure at  $160\text{ }^\circ\text{C}$  for 72 h. The mixture was cooled to room temperature at a rate of  $5\text{ }^\circ\text{C}\cdot\text{h}^{-1}$  and colorless block crystals were obtained in a yield of 45% based on the 4-cpa. Calcd. (%) for  $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{O}_5\text{Pb}$ : C, 34.02; H, 2.48. Found (%): C, 34.11; H, 2.38. IR bands (KBr pellets,  $\text{cm}^{-1}$ ): 3 425 (vs), 2 930(m), 1 543(vs), 1 490(m), 1 423(m), 1 394 (vs), 1 286(s), 1 203(m), 1 180(w), 1 108(w), 1 088(s), 1 014(s), 939(w), 926(m), 858(s), 808(s), 738(s), 685 (s), 586(w), 511(m), 461(m).

### 1.3 Biological activity test

The herbicidal activities of the ligand 4-Hcpa and complex **1** were determined using *Brassica napus* L. and *Digitaria sanguinalis* L. as samples of dicotyledonous and monocotyledonous plants, respectively<sup>[10-11]</sup>. Solutions of the tested compounds were prepared by dissolving them in Dimethyl sulfoxide (100  $\mu\text{L}$ ) with the addition of Tween 20 (2  $\mu\text{L}$ ), and then diluting with distilled water. The germinated seeds were placed on two filter papers in a 9-cm Petri plate, to which 5 mL of tested solution was added in advance. Usually, 15 seeds were used on each plate. The plates were placed in a dark room and allowed to germinate for 72 h at  $25\text{ }^\circ\text{C}$ . The lengths of 10 seed roots selected from each plate were measured and the means were calculated. Moreover, quizalofop-*p*-ethyl, a commercial aryloxy-phenoxy propionate herbicide and the emulsion which does not contain tested compounds were used as control and blank respectively. For all of the bioassay tests, each treatment was repeated three times. Then inhibitory rate was calculated relative to the blank. The bioassay results are shown in Table 4.

### 1.4 Crystal structure determination

A colorless crystal with dimensions of  $0.33\text{ mm}\times 0.27\text{ mm}\times 0.22\text{ mm}$  was selected for X-ray analyses. All diffraction data were collected on a Bruker Smart

Apex II CCD diffractometer operating at 50 kV and 30 mA using a Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073\ \text{nm}$ ) at 296(2) K by using a  $\omega$  scan mode. In the range  $1.58^\circ \leq \theta \leq 25.19^\circ$ , a total of 9 247 reflections were collected, of which 3 179 were unique ( $R_{\text{int}}=0.023\ 4$ ) and 2 950 observed ones ( $I>2\sigma(I)$ ) were used in the succeeding structure calculations. Data collection and reduction were performed using the APEX II software<sup>[12]</sup>. Multi-scan absorption corrections were applied for all the data sets using the SADABS<sup>[12]</sup>. The structure was solved by direct methods and refined by full matrix least squares on  $F^2$  using the SHELXTL program package<sup>[13]</sup>. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms attached to C were added according to theoretical models. Water H atoms were located in difference Fourier maps and refined with distance restraints of O-H 0.082 nm and

H $\cdots$ H 0.139 nm, with a standard deviation of 0.001 nm, and with  $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$ . The final  $R=0.023\ 1$  and  $wR=0.076\ 5$  ( $w=1/[\sigma^2(F_o^2)+(0.064\ 5P)^2+1.806\ 7P]$ , where  $P=(F_o^2+2F_c^2)/3$ ) for 2 950 observed reflections with  $I>2\sigma(I)$ .  $S=1.085$ ,  $(\Delta/\sigma)_{\text{max}}=0.001$ ,  $(\Delta\rho)_{\text{max}}=118.6\ \text{e}\cdot\text{nm}^{-3}$  and  $(\Delta\rho)_{\text{min}}=-904\ \text{e}\cdot\text{nm}^{-3}$ . Crystal parameters and details of the data collection and refinement are given in Table 1. The selected bond lengths and bond angles are shown in Table 2. H-bonding parameters for **1** are given in Table 3.

CCDC: 946824.

## 2 Results and discussion

### 2.1 IR spectra

The IR spectra of complex **1** are recorded as KBr pellets (Fig.1). Strong, broad bands at  $3\ 425\ \text{cm}^{-1}$  may be assigned to  $\nu(\text{O-H})$  of water. The moderate absorption

Table 1 Crystal data and structure refinements of complex **1**

Empirical formula	$\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{O}_3\text{Pb}$	$\gamma / (^\circ)$	72.238 0(10)
Formula weight	564.36	$V / \text{nm}^3$	0.890 05(13)
Temperature / K	296(2)	$Z$	2
Size / mm	0.33×0.27×0.22	$\mu / \text{mm}^{-1}$	9.800
$\theta$ range for data collection / $(^\circ)$	1.58 to 25.19	$D_c / (\text{g}\cdot\text{cm}^{-3})$	2.106
Crystal system	Triclinic	$F(000)$	532
Space group	$P\bar{1}$	Reflections collected	9 247
$a / \text{nm}$	0.726 22(6)	Independent reflections ( $R_{\text{int}}$ )	3 179 (0.023 4)
$b / \text{nm}$	0.999 97(9)	Goodness of fit on $F^2$	1.085
$c / \text{nm}$	1.296 50(11)	$R_1, wR_2$ ( $I>2\sigma(I)$ )	0.023 1, 0.076 5
$\alpha / (^\circ)$	84.078(2)	$R_1, wR_2$ (all data)	0.026 7, 0.097 5
$\beta / (^\circ)$	84.742 0(10)	$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} / (\text{e}\cdot\text{nm}^{-3})$	118.6, -904

Table 2 Selected bond lengths (nm) and angles  $(^\circ)$  for complex **1**

Pb(1)-O(1)	0.251 7(7)	Pb(1)-O(2)	0.254 5(5)	Pb(1)-O(3)	0.251 7(5)
Pb(1)-O(4)	0.245 3(5)	Pb(1)-O(1W)	0.275 8(6)	Pb(1)-O(3) <sup>i</sup>	0.266 7(4)
O(4)-Pb(1)-O(3)	52.03(15)	O(4)-Pb(1)-O(1)	85.59(18)	O(3)-Pb(1)-O(1)	76.34(18)
O(3)-Pb(1)-O(2)	110.54(19)	O(3)-Pb(1)-O(3) <sup>i</sup>	68.53(18)	O(4)-Pb(1)-O(4) <sup>ii</sup>	67.17(19)
O(3) <sup>i</sup> -Pb(1)-O(4) <sup>ii</sup>	145.92(16)	O(4)-Pb(1)-O(1W)	77.32(18)	O(3)-Pb(1)-O(1W)	69.6(2)

Symmetry codes: <sup>i</sup> 1-x, 1-y, -z; <sup>ii</sup> -x, 1-y, -z.

Table 3 Hydrogen bond lengths and angles for complex **1**

D-H $\cdots$ A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
O(1W)-H(1W) $\cdots$ O(2) <sup>ii</sup>	0.082	0.206	0.279 2(4)	150
O(1W)-H(2W) $\cdots$ O(1) <sup>i</sup>	0.082	0.220	0.298 0(3)	159
C(7)-H(7B) $\cdots$ Cl(1) <sup>iv</sup>	0.093	0.283	0.375 3(2)	160

Symmetry codes: <sup>i</sup> 1-x, 1-y, -z; <sup>ii</sup> -x, 1-y, -z; <sup>iv</sup> 1+x, y, z.

band observed at  $2\,930\text{ cm}^{-1}$  is attributed to the  $\nu(\text{C}_{\text{methylene}}\text{-H})$  vibration of 4-cpa ligand. The features at  $1\,543$  and  $1\,490$ ,  $1\,401$ ,  $1\,394\text{ cm}^{-1}$  are associated with the asymmetric (COO) and symmetric (COO) stretching vibrations. The  $\Delta\nu(\nu_{\text{as}}(\text{COO}^-)-\nu_{\text{s}}(\text{COO}^-))$  value are  $53\text{ cm}^{-1}$  (less than  $105\text{ cm}^{-1}$ ) and  $120$ ,  $149\text{ cm}^{-1}$  (between  $200\text{ cm}^{-1}$  and  $105\text{ cm}^{-1}$ ), indicating the coordination of carboxylate with Pb(II) in chelating and bridging modes, respectively<sup>[14]</sup>, which is well consistent with X-ray diffraction structural analysis.

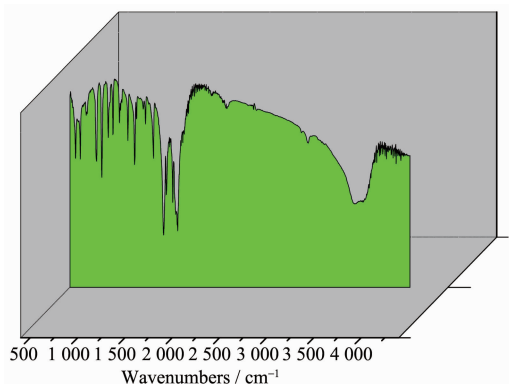
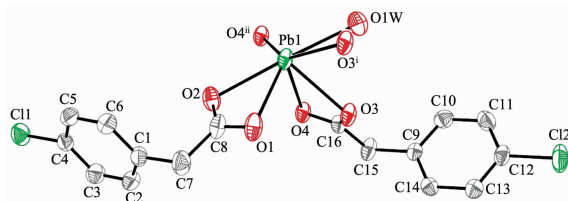


Fig.1 IR spectra of **1**

## 2.2 Structure description

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes with the triclinic space group  $P\bar{1}$  and exhibits a 1D infinite chain structure. A thermal ellipsoid plot of the asymmetry unit of **1** is shown in Fig.2. The Pb(II) ion is seven-coordinated by six carboxylate oxygen atoms from three different 4-cpa ligands and one water molecule, displaying a hemi-directed coordination. The Pb-O bond lengths and O-Pb-O angles, all of which are within the range of those observed for other analogical Pb complexes<sup>[15-16]</sup>, are ranging from  $0.245\,3(5)$  to  $0.275\,8(6)\text{ nm}$  and  $51.80(18)^\circ$  to  $147.45(18)^\circ$ , respectively.

As shown in the scheme, the 4-cpa ligands adopt



30% probability ellipsoids; All hydrogen atoms are omitted for clarity; Symmetry codes: <sup>i</sup>  $1-x, 1-y, -z$ ; <sup>ii</sup>  $-x, 1-y, -z$

Fig.2 Thermal ellipsoids plot of the asymmetric unit of **1**

two different coordination modes: one acts as bridging mode  $\mu_3$  to link three Pb(II) ions, whereas the other has chelating mode linking one Pb(II) ion, differing from this described in  $[\text{pyCu}(\text{4-Cl-C}_6\text{H}_4\text{CH}_2\text{COO})_4\text{-Cupy}]^{[9]}$ , in which the carboxylate group exhibits the same coordination mode of  $\mu_2$  bridging. The carboxylates of 4-cpa connect Pb(II) ions to form an infinite chain parallel to the  $c$ -axis (Fig.3a). Distances between adjacent Pb(II) ions are  $0.428\,5(2)$  and  $0.426\,9(4)\text{ nm}$ , respectively, and the angles among successive Pb(II) is  $116.20(3)^\circ$ . The distances of Pb(1)-O(3) and Pb(1)-O(4) ( $0.266\,7$  and  $0.267\,0\text{ nm}$ ) are longer than Pb(1)-O( $x$ ) ( $x=1\sim 4$ ), which this phenomena may be attributed to the appearance of four-membered ring (Pb1, O4, Pb1<sup>ii</sup> and O4<sup>ii</sup>) between the two Pb(II) ions (symmetry code: <sup>ii</sup>  $-x, 1-y, -z$ ). In the four-membered rings, Pb1, O4, Pb1<sup>ii</sup> and O4<sup>ii</sup> are essentially planar. The C(14)-H(14)  $\cdots \pi$  stacking interactions and C(7)-H(7B)  $\cdots$  Cl(1) hydrogen bonds assemble neighbouring chains into a corrugated layer (Fig.3b). The H-to-centroid distances of H(114)  $\cdots$  Cg(1)<sup>iii</sup> =  $0.277(2)\text{ nm}$  (Cg(1) is the centroid of the C1-C6 ring, symmetry code: <sup>iii</sup>  $-x, 2-y, -z$ ). Moreover, intramolecular O(1W)-H(1W)  $\cdots$

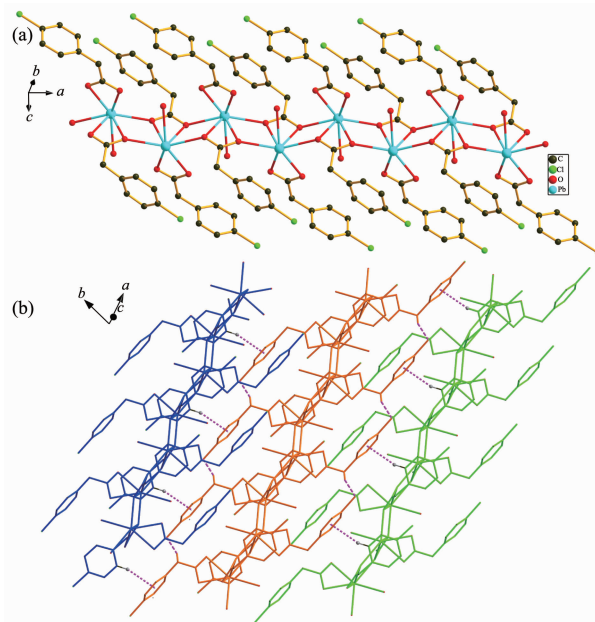


Fig.3 (a) View of the 1D infinite chain of **1** parallel to the  $c$  axis of the unit cell; (b) View of the 2D corrugated layer structure of **1** formed by C-H  $\cdots \pi$  stacking interactions and C-H  $\cdots$  Cl hydrogen bonds (dash lines)

O(2) and O(1W)–H(2W)···O(1) hydrogen bonds are also observed.

### 2.3 Thermal analysis

The thermogravimetric analyses (TGA) of compound **1** were performed in a N<sub>2</sub> atmosphere when the sample was heated to 800 °C at a constant rate of 10 °C·min<sup>-1</sup>. The TG and DTA curves are depicted in Fig.4, which shows that compound **1** has two weight loss steps. The first corresponds to release of one coordinated water molecule from 50~180 °C (Obsd. 3.42%, Calcd. 3.19%). The weight loss step above 260 °C corresponds to the decomposition of framework structure. Finally, **1** was completely degraded into PbO with total loss of 62.71% (Calcd. 60.45%).

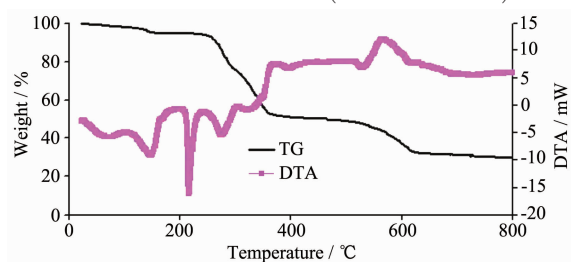


Fig.4 Thermogravimetric curves (DTA and TG) for complex **1**

### 2.4 Powder X-ray diffraction analysis

Samples of complex **1** were measured by X-ray powder diffraction at room temperature. As shown in Fig.5, the peak positions of the experimental patterns are in a good agreement with the simulated patterns, which clearly indicates the good purity of the complex.

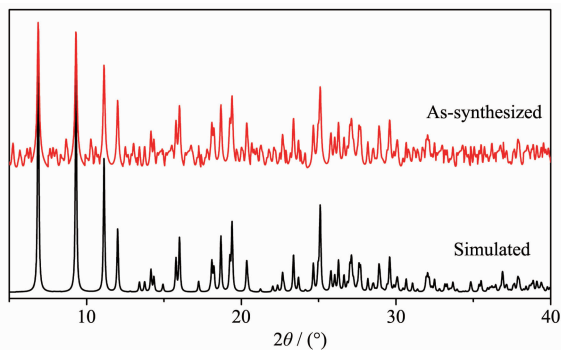


Fig.5 PXRD patterns in complex **1**

### 2.5 Luminescent properties

It has been found that coordination polymers are able to adjust the emission wavelength of organic

ligands by incorporation of metal atoms, so it is of importance to investigate the luminescence properties of coordination polymers in view of potential applications as light-emitting diodes<sup>[17]</sup>. The photo-luminescence of 4-Hcpa and **1** were investigated in the solid state at room temperature. As shown in Fig.6, the emission spectra of the ligand 4-Hcpa and complex **1** exhibit strong emission. The emission maxima ( $\lambda_{em}$ ) of 4-Hcpa and **1** are 356 nm ( $\lambda_{em}$ =297 nm) and 422 nm ( $\lambda_{em}$ =360 nm), respectively. Compared with the free ligand 4-Hcpa, **1** has a red-shift. This red-shift may be caused by ligand-to-metal charge transfer (LMCT) transition, as indicated by previous publications<sup>[18]</sup>, and the emission intensity of complex **1** is clearly enhanced as a result of metal coordination. The luminescent lifetime of solid complex **1** using an Edinburgh FLS920 phosphorimeter with 450 W xenon lamp as excitation source show lifetime for complex **1** of 5.3 ns at 422 nm (Fig.7).

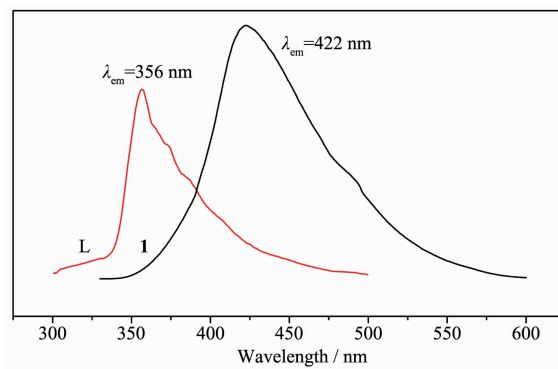


Fig.6 Solid-state emission spectra of 4-Hcpa and complex **1** at room temperature

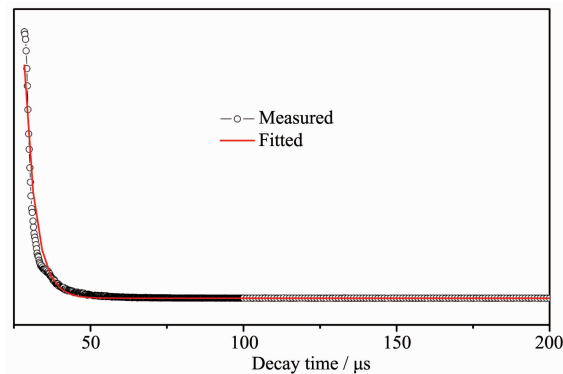


Fig.7 Luminescent lifetime for complex **1** in solid state at room temperature

### 2.6 Biological activities

Aromatic acetic acid, such indole-3-acetic acid



Table 4 Herbicidal activities of 4-Hcpa, complex **1** and quizalofop-P-ethyl

Compounds	Inhibitory rate / %					
	<i>Brassica napus</i> L.			<i>Echinochloa crusgalli</i> L.		
	100 mg·L <sup>-1</sup>	50 mg·L <sup>-1</sup>	10 mg·L <sup>-1</sup>	100 mg·L <sup>-1</sup>	50 mg·L <sup>-1</sup>	10 mg·L <sup>-1</sup>
4-Hcpa	30.6	23.7	10.3	92.1	80.3	42.5
<b>1</b>	34.4	27.8	13.7	95.4	88.3	41.6
quizalofop-p-ethyl	51.2	42.6	30.3	100	95.3	62.1

(IAA), 1-naphthalene acetic acid (1-NAA) are well-known herbicides for weed control<sup>[19]</sup>. 4-Chlorophenylacetate and its complex were chosen as auxin herbicides according to the following considerations: (1) 4-Hcpa belongs to aromatic acetic acid, which maybe exhibit good herbicidal activities; (2) it has been found that the biological activities of ligand maybe activated by metallic ions<sup>[20]</sup>. The herbicidal activities of ligand 4-Hcpa and complex **1** were investigated and shown in Table 4. For 4-Hcpa and **1**, the rates of inhibition of *Brassica napus* L. root growth are 30.6% and 34.4%, 23.7% and 27.8%, 10.3% and 13.7% at concentrations of 100, 50 and 10 mg·L<sup>-1</sup>, respectively, which means that the 4-Hcpa and complex **1** display low herbicidal activities against this plant. However, the rates of inhibition of *Echinochloa crusgalli* L. Root growth are high (92.1% and 95.4%) at a concentration of 100 mg·L<sup>-1</sup>, 80.3% and 88.3% at 50 mg·L<sup>-1</sup>, and 42.5%~41.6% at 10 mg·L<sup>-1</sup>. The results reveal that two samples exhibit excellent herbicidal activities against this kind of weed at 100 and 50 mg·L<sup>-1</sup>, but their activities are not satisfactory at a lower concentration (10 mg·L<sup>-1</sup>). Moreover, we found that complex **1** shows superior effective than ligand 4-Hcpa. It is possible that the ligand 4-Hcpa may be activated by the Pb<sup>2+</sup> ion<sup>[20]</sup>.

### 3 Conclusion

Complex **1** emits the intensely blue luminescence with the fluorescence lifetime of 5.3 ns (422 nm) in the solid state at room temperature. Preliminary bioassay indicates that ligand 4-Hcpa and complex **1** exhibit high herbicidal activities against monocotyledonous plant such as *Echinochloa crusgalli* L. at conc-

entrations of 100 and 50 mg·L<sup>-1</sup>.

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