

Synthesis, Structural Characterization, Fluorescence Properties and Herbicidal Activity of Bis(substituted salicylaldehyde) Carbohydrazone Dibutyltin Complexes^①

FENG Yong-Lan JIANG Wu-Jiu
ZHANG Fu-Xing KUANG Dai-Zhi^②

(Key Laboratory of Functional Metal-organic Compounds of Hunan Province, Key Laboratory of Functional Organometallic Materials of College of Hunan Province, Department of Chemistry and Material Science, Hengyang Normal University, Hengyang, Hunan 421008, China)

ABSTRACT A series of dibutyltin complexes, $(\text{Bu}_2\text{Sn})_2\text{L}$, $[(\text{Bu}_2\text{Sn})_2\text{L}]_3$ and H_2LSnBu_2 , were synthesized by microwave-assisted methanolic solvothermal method, where H_4L is $[2-(\text{OH})-\text{R}-\text{ArCH}=\text{NNH}]_2\text{CX}$, and $\text{X} = \text{O}$, $\text{R} = 4\text{-NEt}_2$ (**T1**), 5-Br (**T2**); $\text{X} = \text{S}$, $\text{R} = \text{H}$ (**T3**); $\text{R} = 5\text{-Br}$ (**T4**). Their structures were characterized by elemental analysis, IR and (^1H , ^{13}C)-NMR spectra. The molecular structure of **T2** was confirmed by X-ray diffraction. The crystal of **T2** belongs to monoclinic system, space group *Ia*. Five-coordinated distorted triangular bipyramids and six-coordinated distorted octahedral configurations were formed by the coordination of oxygen and nitrogen atoms of ligand with two dibutyltins, thus forming a trimeric hexanuclear butyltin complex by the cross coordination of three units $(\text{Bu}_2\text{Sn})_2\text{L}$ with enol imines. The **T2** and **T4** exhibit fluorescence emission in DMF solvents and DMF-water mixture. The fluorescence intensity of **T2**-DMF- H_2O system decreases almost linearly with the increase of water volume fraction (WVF). The aggregation fluorescence enhancement effect of **T4**-DMF- H_2O solution system increases with the increase of WVF at the range of 0~20% WVF. When WVF is more than 20%, the fluorescence intensity decreases with the increase of WVF. In addition, **T1**~**T4** have broad growth activities on target plants, such as *Portulaca oleracea* L., *Amaranthus spinosus* L., *Cassia tora* L., *Brassica campestris* L. *spp. chinensis var. utilis* Tsen et Lee, and *Amaranthus tricolor* L., and can be used as a candidate herbicide for further research.

Keywords: bis(substituted salicylaldehyde) carbohydrazone dibutyltin, fluorescence properties, herbicidal activity; DOI:10.14102/j.cnki.0254-5861.2011-3214

1 INTRODUCTION

Amides widely exist in nature. In organisms, amides of many metal enzymes participate in metal coordination to promote the deprotonation of amides^[1]. As a result, $\text{R}-\text{C}(\text{O})\text{NH}-\text{R}'$ is transformed into nitrogen anion $[\text{R}-\text{C}(\text{O})\text{N}^--\text{R}']$. The deprotonated amide nitrogen atom becomes a good electron donor^[2]. This structural feature of amide compounds plays an important role in the study of coordination chemistry and mechanism of simulated life process. Hydrazides containing $-\text{C}(\text{O})-\text{NH}-\text{NH}_2$ chain-end have primary amino groups, which not only increase the

coordination atoms and coordination modes, but also condense with aldehydes, ketones to produce Schiff bases and metal complexes with biological activity and photoelectric properties^[3-5]. The carbohydrazone or thiocarbohydrazone, as a kind of dihydrazone compound, can condense with salicylaldehyde to produce one- and two-Schiff base compounds with 1,5-symmetric and 1,5-asymmetric bis-salicylaldehyde carbohydrazone, and the amide chain is easier to deprotonate^[6-8]. Because the $\text{C}=\text{N}$ double bond has *cis*- and *trans*-isomerism, the rotation of $\text{C}-\text{N}$ and $\text{N}-\text{N}$ bonds produces space conformational isomerism, and the conversion of amide chain

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② Corresponding author. Tel: 0734-8484932, E-mail: hnkcg@qq.com

[Ar-CH=N-NH-C=O(S)-NH-N=CH-Ar] ketone and enol forms. Therefore, bis(salicylaldehyde) carbohydrazide is a multi-site and multi-mode ligand^[9, 10]. It is of great significance to explore the coordination between ligands with metals, and to synthesize complexes with new structures and properties. In this paper, four ligands of bis(4-diethylamino, 5-bromosalicylaldehyde) carbohydrazide (H_4L^1 , H_4L^2) and bis(salicylaldehyde, 5-bromosalicylaldehyde) thiocarbohydrazide (H_4L^3 , H_4L^4) were prepared by the condensation reaction of salicylaldehyde, 4-diethylamino and 5-bromosalicylaldehyde with carbohydrazide and thiocarbohydrazide, respectively. Four bis(substituted salicylaldehyde) carbohydrazide dibutyltin complexes **T1**~**T4** were synthesized by microwave-assisted solvothermal method. The fluorescence properties of **T(2,4)**-DMF-H₂O system were studied, and the activities of ligands and their complexes **T1**~**T4** on the growth of these plants, such as *Portulaca oleracea* L., *Amaranthus spinosus* L., *Cassia tora* L., *Brassica campestris* L.ssp.*chinensis* var.*utilis* Tsen et Lee and *Amaranthus tricolor* L. were evaluated.

2 EXPERIMENTAL

2.1 Materials and instruments

MicroSYNT Lab station for microwave assisted (Italy). The melting points were obtained on an X-4 microscopic melting point apparatus and uncorrected. ¹H and ¹³C NMR spectra were measured on a Bruker Avance 500 spectrometer (Switzerland) with CDCl₃ as solvent and TMS as an internal standard. IR spectra (4000~400 cm⁻¹ range, KBr discs) were recorded on a Shimadzu FTIR Prestige-21 spectrometer. Elemental analyses of C, H and N were performed with a Perkin-Elmer 2400 II elemental analyzer. Crystal structure was determined on a Bruker Smart Apex II CCD X-ray diffractometer (Germany). F-7000 Fluorescence Spectrometer (Shimadzu). MGC-HP intelligent artificial climate box (Shanghai Yiheng Scientific Instrument Co., Ltd.).

All reagents were purchased from commercial supplies (Energy chemical reagent Co., Ltd; grade: CP) without further purification. Ligands bis(4-diethylaminosalicylaldehyde) carbohydrazide (H_4L^1)^[11], bis(salicylaldehyde) thiocarbohydrazide (H_4L^3)^[12], and bis(5-bromosalicylaldehyde) thiocarbohydrazide (H_4L^4)^[11, 13] were synthesized in our laboratory and characterized by elemental analysis, IR and NMR.

2.2 Preparation of ligand H_4L^2

According to reference^[7, 11], a mixture of 5-bromosalicylaldehyde (40 mmol), carbohydrazide (20 mmol) and ethanol-acetic acid (30 mL, V/V = 7:3) was placed in a 100 mL reactor, then the mixture was stirred and heated to reflux for 6 hours. After cooling down to room temperature, the solution was filtered and the solvent was removed by vacuum evaporation. The crude product was recrystallized from appropriate solvent to yield bis(5-bromosalicylaldehyde) carbohydrazide (H_4L^2), light yellow powder 6.755 g, yield: 74.1%, m.p.: 125~126 °C. Anal. Calcd. (%) for C₁₅H₁₂Br₂N₄O₃: C, 39.50; H, 2.65; N, 12.28. Found (%): C, 39.49; H, 2.66; N, 12.27. IR (KBr): 3235 (m, ν_{O-H}), 3044 (m, ν_{Ar-H}, ν_{N-H}), 1682 (s, ν_{C=O}), 1622 (s, ν_{C=N}) cm⁻¹. ¹H NMR(DMSO-*d*₆, 500MHz) δ (ppm): 11.05 (s, 1H, -OH), 10.98 (s, 1H, -OH), 10.88 (s, 2H, -NH-), 9.01 (s, 1H, -CH=N), 8.94 (s, 1H, -CH=N), 6.85~8.50 (m, 6H, Ar-H).

2.3 Syntheses of the complexes

A mixture of 1 mmol ligand, 2 mmol dibutyltin oxide, and 15 mL anhydrous methanol was placed in a 50 mL Teflon-lined reactor. The reactants are stirred and the reactor is sealed, and set on the microwave power 800 W, 120 °C of MicroSYNT Lab station for microwave assisted synthesis. The mixture was heated by microwave radiation for two hours. The reactants were naturally cooled down to room temperature. Then the solution was obtained by filtration, and the filtrate was removed by evaporation in vacuo. Crystals of the complexes were obtained by recrystallization from methanol. The yield was calculated based on ligand.

T1, brownish yellow crystal, 0.626 g. Yield: 69.4%, m.p.: 167~168 °C. Anal. Calcd. (%) for C₃₉H₆₄N₆O₃Sn₂: C, 51.91; H, 7.15; N, 9.31. Found (%): C, 51.92; H, 7.15; N, 9.30. IR: 3019 (s, ν_{Ar-H}), 2922 (m, ν_{C-H}), 1620 (s, ν_{C=N}), 573 (m, ν_{Sn-O}), 538 (s, ν_{Sn-O}), 453 (s, ν_{Sn-N}), 432 (s, ν_{Sn-C}) cm⁻¹. ¹H NMR (CDCl₃) δ (ppm): 8.17 (s, 1H, -CH=N), 7.66 (s, 1H, -CH=N), 5.97~6.90 (m, 6H, Ar-H), 3.35~3.37 (m, 8H, -NCH₂-), 0.84~1.69 (m, 48H, -CH₂CH₃). ¹³C NMR (CDCl₃) δ (ppm): 166.74, 166.64, 165.22 (-C=N), 155.08, 152.24, 152.22, 147.32, 107.55, 106.84, 102.85, 102.77, 100.91, 100.56(Ar-C), 27.50, 27.35, 27.20, 26.89, 26.60, 26.51, 26.24, 22.34, 22.13(-CH₂-), 13.66, 13.59, 12.84, 12.81, 12.69 (-CH₃).

T2, golden yellow crystal, 0.484 g. Yield: 70.5%, m.p.: 193~194 °C. Anal. Calcd. (%) for C₉₃H₁₃₂Br₆N₁₂O₉Sn₆: C, 40.56; H, 4.83; N, 6.10. Found (%): C, 40.55; H, 4.87; N, 6.11. IR: 2918 (m, ν_{Ar-H}), 2851 (m, ν_{C-H}), 1599 (s, ν_{C=N}), 584

(s, $\nu_{\text{Sn-O}}$), 546 (s, $\nu_{\text{Sn-O}}$), 465 (s, $\nu_{\text{Sn-N}}$), 448 (s, $\nu_{\text{Sn-C}}$) cm^{-1} . ^1H NMR (CDCl_3) δ (ppm): 8.38 (s, 1H, $-\text{CH}=\text{N}$), 8.32 (s, 1H, $-\text{CH}=\text{N}$), 8.28 (s, 1H, $-\text{CH}=\text{N}$), 8.01 (s, 1H, $-\text{CH}=\text{N}$), 7.83 (s, 1H, $-\text{CH}=\text{N}$), 7.72 (s, 1H, $-\text{CH}=\text{N}$), 6.59~7.30 (m, 18H, Ar-H), 1.31~1.65 (m, 72H, $-\text{CH}_2-$), 0.84~0.87 (m, 36H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3) δ (ppm): 163.54, 162.59 ($-\text{C}=\text{N}$), 136.17, 135.93, 134.59, 133.91, 133.56, 133.36, 132.26, 123.46, 123.19, 122.89, 121.59, 118.94, 117.27 (Ar-C), 27.29, 26.81, 26.78, 26.57, 26.49, 26.25, 22.84, 22.80, 22.72, 22.60, 22.55, 22.47 ($-\text{CH}_2-$), 13.62, 13.59, 13.57 ($-\text{CH}_3$).

T3, yellow crystal, 0.416 g. Yield: 76.3%, m.p.: 215~216 °C. Anal. Calcd. (%) for $\text{C}_{23}\text{H}_{30}\text{O}_2\text{N}_4\text{SSn}$: C, 50.66; H, 5.55; N, 10.27. Found (%): C, 50.67; H, 5.54; N, 10.27. IR: 3150 (m, $\nu_{\text{O-H}}$), 3019 (m, $\nu_{\text{N-H}}$), 2959 (m, $\nu_{\text{Ar-H}}$), 2913 (m, $\nu_{\text{C-H}}$), 1607 (s, $\nu_{\text{C=N}}$), 540 (w, $\nu_{\text{Sn-O}}$), 502 (w, $\nu_{\text{Sn-N}}$), 475 (w, $\nu_{\text{Sn-C}}$), 440 (w, $\nu_{\text{Sn-S}}$) cm^{-1} . ^1H NMR (CDCl_3) δ (ppm): 11.13 (s, 1H, $-\text{OH}$), 8.72 (s, 1H, $-\text{CH}=\text{N}$), 8.59 (s, 1H, $-\text{CH}=\text{N}$), 7.90 (s, 1H, $-\text{N-H}$), 6.70~7.32 (m, 8H, Ar-H), 1.31~1.69 (m, 12H, $-\text{CH}_2$), 0.88 (t, 6H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3) δ (ppm): 166.97, 166.55, 164.71, 162.74, 159.75, 157.69 ($-\text{C}=\text{N}$), 143.73, 135.22, 133.89, 133.45, 132.56, 130.93, 129.95, 121.51, 119.75, 119.35, 117.94, 117.13, 117.17, 117.05, 116.81 (Ar-C), 27.52, 27.39, 27.27, 26.52, 26.23 ($-\text{CH}_2-$), 13.62 ($-\text{CH}_3$).

T4, brownish yellow crystal, 0.569 g. Yield: 80.9%, m.p.: 173~174 °C. Anal. Calcd. (%) for $\text{C}_{23}\text{H}_{28}\text{Br}_2\text{N}_4\text{O}_2\text{SSn}$: C, 39.29; H, 4.01; N, 7.97. Found (%): C, 39.28; H, 4.02; N, 7.98. IR: 3140 (m, $\nu_{\text{O-H}}$), 2955 (m, $\nu_{\text{N-H}}$), 2924 (m, $\nu_{\text{Ar-H}}$), 2874 (m, $\nu_{\text{C-H}}$), 1589 (s, $\nu_{\text{C=N}}$), 546 (w, $\nu_{\text{Sn-O}}$), 469 (w, $\nu_{\text{Sn-N}}$), 444 (w, $\nu_{\text{Sn-C}}$), 413 (w, $\nu_{\text{Sn-S}}$) cm^{-1} . ^1H NMR (CDCl_3) δ (ppm): 11.13 (s, 2H, $-\text{OH}$), 8.59 (s, 2H, $-\text{CH}=\text{N}$), 7.90 (s, 2H, $-\text{N-H}$), 6.70~7.32 (m, 12H, Ar-H), 1.32~1.69 (m, 24H, $-\text{CH}_2$), 0.88 (t, 12H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3) δ (ppm): 166.98, 165.92, 161.36, 156.65 ($-\text{C}=\text{N}$), 142.19, 137.67, 135.11, 133.50, 131.95, 123.46, 119.58, 118.99, 118.20, 110.95, 108.02 (Ar-C), 27.35, 27.23, 26.49, 26.41 ($-\text{CH}_2-$), 13.61 ($-\text{CH}_3$).

2.4 Crystal structure determination of T2

The crystal of **T2** with dimensions of 0.13mm \times 0.12mm \times 0.10mm was selected. The crystal data were collected by a Bruker Smart Apex II CCD diffractometer (MoK α radiation, $\lambda = 0.71073$ Å) in the ranges of $1.96 \leq \theta \leq 29.53^\circ$; $-34 \leq h \leq 27$, $-14 \leq k \leq 22$ and $-36 \leq l \leq 36$. A total of 29020 reflections were collected and 18877 were independent ($R_{\text{int}} = 0.0323$), of which 16160 observed reflections with $I > 2\sigma(I)$ were used in the succeeding refinements. The

structure was solved by direct methods with SHELXS program and refined by full-matrix least-squares technique using the SHELXL^[14]. Hydrogen atoms were placed in calculated positions or located from difference Fourier maps, and refined isotropically with isotropic vibration parameters related to the non-hydrogen atom to which they are bound. All calculations were performed with SHELXTL program. Empirical formula, $\text{C}_{93}\text{H}_{132}\text{Br}_6\text{N}_{12}\text{O}_9\text{Sn}_6$, 2753.71 g/mol, monoclinic system, space group *Ia*, $a = 25.0359(11)$, $b = 16.8398(6)$, $c = 26.665(2)$ Å, $\beta = 112.443(5)^\circ$, $V = 10390.5(10)$ Å³, $T = 293(2)$ K, $Z = 4$, $D_c = 1.760$ Mg/m³, $\mu = 3.786$ mm⁻¹ and $F(000) = 5424$. A full-matrix least-squares refinement gave the final $R = 0.0415$, $wR = 0.1005$ ($w = 1/[\sigma^2(F_o^2) + (0.0630P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$, $S = 1.036$, $(\Delta\rho)_{\text{max}} = 1.414$ and $(\Delta\rho)_{\text{min}} = -0.842$ e/Å³).

2.5 Determination of herbicidal activity

The herbicidal activities of the ligands and their complexes were evaluated by plating method^[7]. The root and stem lengths of the target plants, such as *Portulaca oleracea* L., *Amaranthus spinosus* L., *Cassia tora* L., *Brassica campestris* L. ssp. *chinensis* var. *utilis* Tsen et Lee and *Amaranthus tricolor* L., were determined. Each treatment was repeated thrice and the growth inhibition rate (*I*) of target plants was calculated by comparing the difference between the average plant growth length (l_0) of water as a reference solution and the average plant growth length (l_1) of the treated plants compared with the l_0 value. If *I* is positive, the ligand or complex has inhibitory effect on target plants, while when *I* is negative, it can promote the target plants.

$$I = \frac{l_0 - l_1}{l_0} \times 100\%$$

3 RESULTS AND DISCUSSION

Our previous research and comparison show that microwave irradiation method has the advantages of fast reaction, high yield, convenient operation and environment-friendly. It is better than the conventional heating method^[15].

3.1 Spectral characteristics

The interaction between bis(salicylaldehyde) carbohydrazide or thiocarbohydrazide and metal may produce mononuclear and binuclear complexes. The characteristic spectra of hydroxyl group (O-H), carbonyl ($>\text{C}=\text{O}$) and metal coordinated Sn-N(O) are important information to distinguish their structural changes. For example, the H_4L^1 and H_4L^2 have absorption peak, with a strong, wide peak of

hydroxyl $\nu_{(\text{O-H})}$ at 3273, 3235 cm^{-1} , and a very strong peak of carbonyl $\nu_{(\text{C=O})}$ at 1707 and 1682 cm^{-1} , respectively. But these characteristic peaks disappeared in **T1** and **T2**, and the strong characteristic absorption peaks of $\nu_{(\text{C=N})}$ were weakened obviously. Also, in the low field of ^1H NMR spectra, the proton peaks of phenolic hydroxyl group (**O-H**) and amide (**>N-H**) disappeared, and weak characteristic peaks of $\nu_{(\text{Sn-O})}$, $\nu_{(\text{Sn-N})}$ and $\nu_{(\text{Sn-C})}$ appeared in the infrared spectra of the complexes^[16, 17]. These changes of spectral characteristics support each other, indicating binuclear complexes **T1** and **T2**. The characteristic peaks of thiocarbonyl (**>C=S**) at 1272 (H_4L^3) and 1277 cm^{-1} (H_4L^4) disappear in **T3** and **T4**, respectively, and the absorption peaks of $\nu_{(\text{C=N})}$ are weakened. However, the moderate and wide infrared characteristic absorption peaks of $\nu_{(\text{O-H})}$ and the proton peaks of low-field phenol hydroxyl (**O-H**) and amino (**>N-H**) did not disappear, and weak characteristic peaks of $\nu_{(\text{Sn-O})}$, $\nu_{(\text{Sn-N})}$ and $\nu_{(\text{Sn-C})}$ were produced^[15], and $\nu_{(\text{Sn-S})}$ weak peaks were also produced in **T3** and **T4**^[18], which indicated that the mononuclear complexes **T3** and **T4** were formed by the coordination of ligands with tin. These ^{13}C NMR data of the complexes further support the structures.

3.2 Crystal structure of T2

Bis(brominated salicylaldehyde) carbohydrazides have seven atoms of nitrogen and oxygen, which may coordinate

with metal. The hydrogen on amide nitrogen is transferred to oxygen of carbonyl **>C=O**, resulting in the conversion of ketone form to enol^[16, 19], and the enolation form conjugated with **C=N**, aromatic rings. X-ray diffraction analysis shows that a phenoxy, imine N and dehydrogenated nitrogen of the bis(brominated salicylaldehyde) carbohydrazide coordinate with dibutyltin to form one unit, $(\text{Bu}_2\text{Sn})_2\text{L}$. The bond lengths and bond angles between the tin atom and ligand are different. Five-coordinated distorted triangular bipyramids and six-coordinated distorted octahedral configurations are formed in a unit structure, respectively. Interestingly, the nitrogen atom which is dehydrogenated from one unit interacts with the tin atom of another unit to form a trimer complex, $[(\text{Bu}_2\text{Sn})_2\text{L}]_3$. The three six-coordinated tin atoms Sn(2), Sn(4) and Sn(6) are located in the core to form a small triangle. Three five-coordinated tin atoms Sn(1), Sn(3) and Sn(5) form a large triangle at the outer. The small triangle is inverted in the large triangle to form a spatial skeleton structure. The plane angle of the two triangles is 0.00°, and six tin atoms are coplanar. The plane of six benzene rings is obviously deviated from the plane of these tin atoms, forming a "propeller" like structure. The crystal molecular structure of the complex is shown in Fig. 1, and its bond parameters are shown in Table 1.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) of T2

Bond	Dist.	Bond	Dist.	Bond	Dist.
Sn(1)–O(1)	2.084(6)	Sn(3)–N(7)	2.231(7)	Sn(6)–O(8)	2.291(6)
Sn(1)–N(1)	2.182(7)	Sn(4)–O(5)	2.081(6)	Sn(6)–N(12)	2.359(7)
Sn(1)–N(3)	2.219(7)	Sn(4)–O(6)	2.317(6)	Sn(6)–N(2)	2.486(7)
Sn(2)–O(2)	2.086(6)	Sn(4)–N(8)	2.387(7)	N(1)–N(2)	1.374(10)
Sn(2)–O(3)	2.337(6)	Sn(4)–N(10)	2.453(7)	N(3)–N(4)	1.410(9)
Sn(2)–N(4)	2.370(7)	Sn(5)–O(7)	2.076(6)	N(5)–N(6)	1.394(9)
Sn(2)–N(6)	2.451(7)	Sn(5)–N(9)	2.176(7)	N(7)–N(8)	1.355(10)
Sn(3)–O(4)	2.089(6)	Sn(5)–N(11)	2.227(7)	N(9)–N(10)	1.372(10)
Sn(3)–N(5)	2.191(7)	Sn(6)–O(9)	2.087(6)	N(11)–N(12)	1.373(10)
Angle	(°)	Angle	(°)	Angle	(°)
O(1)–Sn(1)–N(1)	84.3(2)	C(24)–Sn(2)–N(6)	87.6(4)	O(7)–Sn(5)–N(9)	83.1(3)
C(20)–Sn(1)–N(1)	113.3(3)	O(3)–Sn(2)–N(6)	132.9(2)	O(7)–Sn(5)–N(11)	153.6(3)
C(16)–Sn(1)–N(1)	121.1(3)	N(4)–Sn(2)–N(6)	157.4(2)	N(9)–Sn(5)–N(11)	71.4(3)
O(1)–Sn(1)–N(3)	155.4(2)	O(4)–Sn(3)–N(5)	82.9(2)	O(9)–Sn(6)–O(8)	145.7(2)
C(20)–Sn(1)–N(3)	97.3(3)	O(4)–Sn(3)–N(7)	150.6(2)	O(9)–Sn(6)–N(12)	77.9(2)
C(16)–Sn(1)–N(3)	100.5(3)	N(5)–Sn(3)–N(7)	71.4(3)	O(8)–Sn(6)–N(12)	68.3(2)
N(1)–Sn(1)–N(3)	71.1(3)	O(5)–Sn(4)–O(6)	145.7(2)	C(86)–Sn(6)–N(2)	81.3(4)
O(2)–Sn(2)–O(3)	145.9(2)	O(5)–Sn(4)–N(8)	78.0(2)	O(9)–Sn(6)–N(2)	81.9(2)
O(2)–Sn(2)–N(4)	78.2(2)	O(6)–Sn(4)–N(8)	68.2(2)	O(8)–Sn(6)–N(2)	132.2(2)
O(3)–Sn(2)–N(4)	68.8(2)	O(5)–Sn(4)–N(10)	82.1(2)	N(12)–Sn(6)–N(2)	159.5(2)
O(2)–Sn(2)–N(6)	80.9(2)	O(6)–Sn(4)–N(10)	132.1(2)		
C(28)–Sn(2)–N(6)	86.6(4)	N(8)–Sn(4)–N(10)	159.3(2)		

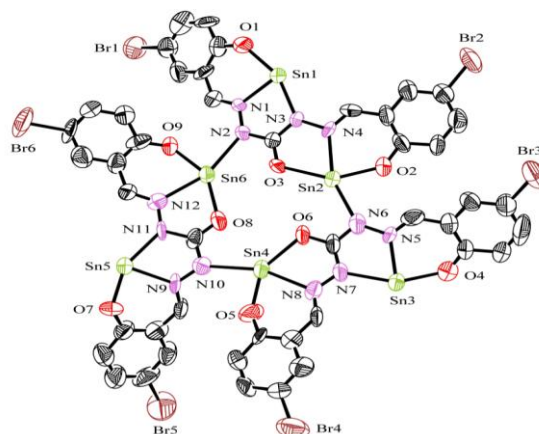


Fig. 1. Molecular structure of **T2** (butyls and H atoms are omitted for clarity)

3.3 Fluorescence properties of

T(2,4)-DMF-H₂O system

It has been found that some organic small molecules, in good solvent, compound displayed very weak fluorescence, while strong emission was observed when they were placed in poor solvent. The solution produces an enhanced aggregation fluorescence (AEE) effect^[20, 21]. We also found this luminescence phenomenon in DMF solution of organotin complex^[22]. In order to search for luminescent materials, **T2** and **T4**-DMF-H₂O (V:V) solutions with concentration of 0.363 (**T2**) and 1.422 (**T4**) $\mu\text{M L}^{-1}$ were prepared respectively. The UV-Vis absorption spectra of **T(2,4)**-DMF-H₂O solution were measured when the volume ratio of DMF to water was 7:2. The fluorescence emission spectra of **T(2,4)**-DMF-H₂O with different water volume fractions (WVF) were measured by fluorescence spectrometer, and the influence of water on the fluorescence intensity of solution system was explored. The results are

shown in Fig. 2. There is a fluorescence emission peak at 402 nm in DMF solution of **T2**. When a certain amount of water is added into **T2**-DMF solution, the fluorescence intensity almost linearly decreases with the increase of WVF. When the water content reaches 90%, there is almost no fluorescence. However, when carbonylhydrazide was replaced by thiocarbonylhydrazide, the fluorescence intensity of the complex **T4**-DMF-H₂O solution increases with the increase of WVF, and gets to the maximum when the WVF reaches 20%, which indicates that the **T4**-DMF-H₂O system has the aggregation fluorescence enhancement effect at the WVF of 0~20%^[20]. Then, with the increase of WVF, the fluorescence intensity decreases, and finally fluorescence quenching occurs. Maybe due to the increase of water content, the solution system is unstable, thus resulting in the loss of aggregation fluorescence enhancement effect, which provides a reference for further research on the aggregation-induced fluorescence materials of complexes.

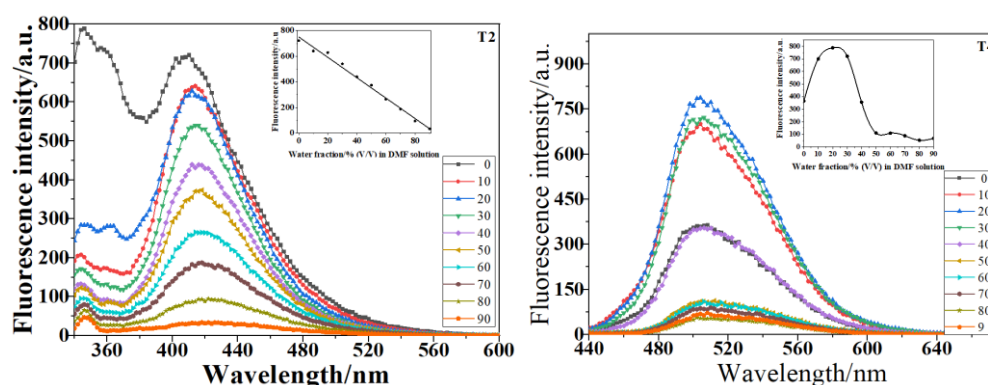


Fig. 2. Fluorescence spectra of **T2** and **T4** in DMF-H₂O with different WVF

(Inset shows a plot of maximum fluorescence intensity of complex in DMF-H₂O mixtures with different WVF)

3.4 Herbicidal activity

The effects of ligands (H₄L) and their complexes (**T**) on

the growth of roots (R) and stems (S) of five target plants, such as, *Portulaca oleracea* L., *Amaranthus spinosus* L.,

Cassia tora L., *Brassica campestris* L.ssp.*chinensis* var.*utilis* Tsen et Lee and *Amaranthus tricolor* L. were investigated. As shown in Table 2, the bioactivity of organotin compounds is related to the groups and ligands attached to tin. It can be seen from Table 2 that, except H_4L^1 and **T1**, H_4L^2 and **T2** which have few effects on *Amaranthus spinosus* L. and *Brassica campestris* L.ssp. *chinensis* var. *utilis* Tsen et Lee respectively, the ligands and their complexes have effects on the growth of target plants^[12]. However, in the concentration range of the test solution, most of the ligands (except H_4L^1 which has a greater effect on *Cassia tora* L.) have less effects. For the same target plant, the complex has a greater growth inhibition than its ligand. With the increase of concentration, the effect of the complexes on target plants increased^[12, 16]. When the concentration of the test solution was 100 mg/L, the inhibition rate (*I*) of most target plants was almost 100%. The inhibition rate of **T1** on the root growth of *Amaranthus spinosus* L. was 28% at the test

concentration of 50 mg/L. When one butyl of **T1** was replaced by chlorine atom, the inhibition rate on the root growth of *Amaranthus spinosus* L. was 70%. If the carbonyl oxygen of ligand was replaced by sulfur atom and one butyl was substituted by chlorine atom, the inhibition rate on the root growth of *Amaranthus spinosus* L. was 100%^[11].

It is significant that H_4L^3 , **T3** and H_4L^4 , **T4** have negative inhibition rate (*I*) on the growth of *Brassica campestris* L.ssp.*chinensis* var.*utilis* Tsen et Lee and *Amaranthus spinosus* L. respectively, and promote the growth of *Brassica campestris* L. ssp. *chinensis* var. *utilis* Tsen et Lee and *Amaranthus spinosus* L.. It is possible that the sulfur-containing organic compounds have special effects on the growth of *Brassica campestris* L.ssp.*chinensis* var.*utilis* Tsen et Lee and *Amaranthus spinosus* L.. Therefore, the title complexes **T1~T4** have broad activities on the growth of target plants, and can be used as candidate herbicides for further study.

Table 2. Inhibition Rate (*I*%) of Ligand (H_4L) and Its Complex (T**) on Plant Roots (**R**) and Stem (**S**)**

	Po		As		Bc		At		Ct	
	R	S	R	S	R	R	S	R	S	R
c(mg/L)	H_4L^1 / T1									
10	14/12	12/14	11/12	10/16	24/11	22/17	14/16	22/21	14/42	12/44
25	24/24	22/22	23/26	15/23	54/28	42/30	24/29	32/32	23/74	22/72
50	35/23	23/36	27/28	18/39	85/36	85/38	25/33	33/39	35/100	23/100
100	37/46	35/68	32/53	22/58	100/100	100/100	30/100	37/100	37/100	35/100
150	42/88	41/89	37/44	27/55	100/100	100/100	40/100	40/100	42/100	41/100
200	39/100	36/100	39/56	30/62	100/100	100/100	37/100	40/100	39/100	36/100
c(mg/L)	H_4L^2 / T2									
10	8/28	7/36	10/37	12/33	9/45	8/26	5/10	7/14	10/33	11/35
25	10/58	12/53	11/79	13/66	11/64	10/54	6/12	11/22	14/64	12/66
50	13/77	15/76	17/98	15/89	11/87	18/89	11/22	13/26	16/79	15/82
100	15/97	13/99	19/100	16/97	13/99	25/98	14/24	14/28	18/96	16/97
150	16/100	15/100	22/100	15/100	15/100	30/100	17/35	16/39	19/100	15/100
200	16/100	16/100	24/100	17/100	17/100	32/100	22/37	15/44	20/100	17/100
c(mg/L)	H_4L^3 / T3									
10	16/38	16/37	31/46	32/46	24/60	24/61	-15/-30	-16/-30	17/54	16/55
25	32/79	32/81	35/76	36/76	45/85	45/85	-33/-47	-34/-49	24/87	24/90
50	44/98	44/99	46/88	45/89	55/98	55/97	-45/-69	-34/-71	33/99	34/100
100	45/100	47/100	56/98	57/100	67/100	67/100	-60/-60	-59/-59	46/100	46/100
150	52/100	52/100	64/100	64/100	70/100	70/100	-62/-60	-64/-60	58/100	59/100
200	56/100	56/100	67/100	67/100	72/100	72/100	-63/-57	-63/-60	58/100	59/100
c(mg/L)	H_4L^4 / T4									
10	2/33	-1/35	-24/-31	-15/-38	2/43	12/36	2/33	0/36	2/24	-1/26
25	5/77	5/86	-13/-47	-8/-36	3/77	11/86	0/46	0/87	5/57	5/52
50	3/100	6/100	-7/-44	-4/-40	4/100	14/100	1/77	0/80	3/78	6/80
100	3/100	5/100	13/-56	15/-57	10/100	10/100	0/97	2/100	3/100	5/100
150	4/100	2/100	45/-38	46/-46	13/100	10/100	4/100	2/100	4/100	2/100
200	10/100	7/100	67/-45	57/-60	17/100	15/100	3/100	2/100	10/100	7/100

Note: the abbreviations of symbols are: R plant roots, S plant stems; Po *Portulaca oleracea* L., As *Amaranthus spinosus* L., Ct *Cassia tora* L., Bc *Brassica campestris* L. ssp. *chinensis* var. *utilis* Tsen et Lee and At *Amaranthus tricolor* L.

4 CONCLUSION

A series of bis(substituted salicylaldehyde) carbohydrazide dibutyltin complexes were synthesized by the reaction of dibutyltin oxide with bis(substituted salicylaldehyde) carbohydrazide or thiocarbohydrazide in the microwave methanol solvothermal method. Complexes **T2** and **T4** have good fluorescence properties in DMF-H₂O solution system.

When the water volume fraction of **T4**-DMF-H₂O system is 0~20%, it has the effect of aggregation fluorescence enhancement. The complexes have good activity on five target plants of *Portulaca oleracea* L., *Amaranthus spinosus* L., *Cassia tora* L., *Brassica campestris* L.ssp.chinensis var.utilis Tsen et Lee and *Amaranthus tricolor* L. These complexes can be used as candidate compounds of herbicides for further study.

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