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# A new off-on fluorescent sensor for the detection of Al(III) based on a chromone-derived Schiff-base

Li-mei Liu, Zheng-yin Yang\*

College of Chemistry and Chemical Engineering, State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P.R. China \*Corresponding author. Tel: +86 931 8913515; Fax: +86 931 812582; e-mail: yangzy@lzu.edu.cn (Z.Y. Yang)

#### Abstract

A new Al<sup>3+</sup> sensor, 6-ethoxychromone-3-carbaldehyde-(3-hydroxy-2-naphthalene acyl) hydrazone (L), was designed and synthesized. The sensor L could exist steadily and detect Al<sup>3+</sup> in the pH range from 5.0 to 8.0 in ethanol and water (3:1, v/v). This sensor showed good selectivity and high sensitivity towards Al<sup>3+</sup> in the presence of most metal ions, and a remarkable enhancement in fluorescence emission intensity at 508nm ( $\lambda_{ex}$ =420nm) was observed with addition of 1equiv Al<sup>3+</sup>, which was attributed to the inhibition of photoinduced electron-transfer (PET) phenomenon and C=N isomerization process. With the fluorescence titration experiments and the ESI-MS spectrum data, we reached the conclusion that the binding ratio between L and Al<sup>3+</sup> was 2:1. Besides, the binding constant (K<sub>a</sub>) between L and Al<sup>3+</sup> was calculated to be 9.24×10<sup>3</sup> M<sup>-1</sup> and the detection limit of L for Al<sup>3+</sup> was as low as 1.82×10<sup>-7</sup>M.

Key Words: Fluorescent sensor; Aluminum ion; PET; C=N isomerization

#### Introduction

Among metals, aluminum is the most prevalent (8.3% by weight) metallic element and the third most abundant of all elements (after oxygen and silicon) in the earth's crust. It is extensively used in many fields, from industrial fields (water treatment, food additives, medicines) to our daily life (various packing items, electrical equipment) [1-8]. Aluminum also plays a great role in biochemical reactions, such as enzyme-catalyzed reactions, biotechnological transformation [9-10]. But mounting evidences suggest that excessive absorption of aluminum is harmful to human health. It sometimes leads to diseases, such as Alzheimer's disease, Parkinson's disease, Osteoporosis and Osteomalacia [11-16]. According to the World Health Organization (WHO) report, the average daily human intake of aluminum is around 3–10 mg and the concentration of Al<sup>3+</sup> in drinking water should not exceed 200mg/L [17-18]. Hence, it is of great importance to develop the efficient methods for the detection of aluminum in organism and environment.

Fluorescent sensors, owing to their visual simplicity, high sensitivity, inexpensive apparatus, instantaneous response, real-time detection, and nondestructive properties, have been one of the most convenient methods to detect metal ions [19-20]. What's more, fluorescence detection has been widely used in enormous fields such as analytical chemistry, environment biology, biochemistry and medical science [21-24]. Nevertheless, because of the poor coordination ability, strong hydration ability, and lack of spectroscopic properties of Al<sup>3+</sup>, it is more

difficult to develop fluorescent sensors for sensing Al<sup>3+</sup> compared with recognizing transition metal ions. In general, as Al<sup>3+</sup> is a hard-acid, it has been found that Al<sup>3+</sup> prefers to coordinate with hard-base donor sites like N and O atoms [25-29]. Moreover, Schiff-bases are well known as hard bases which can provide nitrogen-oxygen-rich coordination environments for Al<sup>3+</sup>. As a consequence, a large number of Schiff-bases can be used as Al<sup>3+</sup> probes [30-33].

In the present work, we report a new chromone Schiff-base as a fluorescence "off-on" sensor for the detection of Al<sup>3+</sup> in ethanol and water (3:1, v/v). Its synthetic route is shown in Scheme1 and characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, ESI-MS and HR-MS. The free sensor shows no fluorescence emission. Upon binding of Al<sup>3+</sup>, L exhibits a significant fluorescence emission in ethanol and water (3:1, v/v). Besides, the sensor shows good selectivity and high sensitivity towards Al<sup>3+</sup> in the presence of most metal ions.

#### Experimental

#### Materials and apparatus

All chemicals were purchased from commercial suppliers and used without further purification. The solutions of metal ions were performed from their nitrate salts. <sup>1</sup>H NMR spectra were measured on the Bruker 300MHz instruments using TMS as an internal standard and DMSO-d<sub>6</sub> as a solvent. <sup>13</sup>C NMR spectrum was measured on the Bruker 400MHz instruments using DMSO-d<sub>6</sub> as a solvent. ESI-MS were determined on a Bruker esquire 6000 spectrometer using DMF as solvent. HR-MS

spectrum was obtained on high resolution mass spectrometer (LTQ-Obitrap-ETD) in DMF. Fluorescence spectra were recorded on a Hitachi RF-4500 spectrophotometer. UV-Vis absorption spectra were determined on a Shimadzu UV-240 spectrophotometer. FTIR spectra were collected on a VERTEX 70V instrument. The melting point was determined on a Beijing XT4-100x microscopic melting point apparatus. All pH measurements were carried out on a FE28 acidometer.

#### Synthesis

6-ethoxychromone-3-carbaldehyde was obtained according to the literature procedures [34]. Synthesis of L was based on the following method (**Scheme 1**): an ethanol solution (10mL) of 3-hydroxy-2-naphthoic acid hydrazide (0.1011 g, 0.5mmol) was added dropwise to a solution of 6-ethoxy chromone-3-carbaldehyde (0.1091g, 0.5mmol) in ethanol (10mL). Then the solution was refluxed for 6 hours under stirring and some white precipitant appeared. The mixture was filtered and dried under vacuum. Yield: 95.4%, Melting point: 213–214 °C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300MHz) δ (ppm): 12.09 (s, 1H, -NH-), 11.27 (s, 1H, -OH-), 8.86 (s, 1H, H<sup>9</sup>), 8.64 (s, 1H, H<sup>2</sup>), 8.45 (s, 1H, H<sup>15</sup>), 7.91 (d, 1H, *J*=7.9Hz, H<sup>14</sup>), 7.76 (d, 1H, *J*=8.0Hz, H<sup>11</sup>), 7.71 (d,1H, *J*=9.0Hz, H<sup>4</sup>), 7.54-7.32 (m, 5H, H<sup>5,7,10,12,13</sup>), 4.52 (q, 2H, -CH2-), 1.38 (t, 3H, -CH3) (**Figure.S2**). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 400MHz) δ(ppm): 161.17, 153.82, 145.47, 144.06, 143.95, 140.80, 133.71, 129.19, 124.35, 123.30, 123.02, 121.85, 121.09, 119.76, 119.57, 119.42, 116.62, 116.12, 114.43, 108.96, 105.12, 71.63, 31.97 (**Figure.S3**). MS (ESI) 403.1 [M+H]<sup>+</sup>, 425.1 [M+Na]<sup>+</sup>, (**Figure.S4**). HR-MS 403.13

[M+H]<sup>+</sup>, 425.11 [M+Na]<sup>+</sup>, (**Figure.S5**).



**Scheme 1.** The synthetic route of 6-ethoxychromone-3-carbaldehyde-(3-hydroxy-2-naphthalene acyl) hydrazone (L).

#### Analysis

Stock solutions (5.0mM) of the nitrate salts of Na<sup>+</sup>, K<sup>+</sup>, Ag<sup>+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup> were prepared in ethanol. Stock solutions of L (5.0mM) were prepared in DMF. The solution of L was then diluted to 50.0 $\mu$ M in ethanol and water (3:1, v/v). In experiments, each time 2mL solution of L (50.0 $\mu$ M) was filled in the quartz optical cell of 1 cm optical path length, and the ions stock solution were added into the quartz optical cell gradually by using a pipette. The excitation and emission slit widths were 3.0nm and 5.0nm respectively.

#### **Results and discussion**

#### **Absorption studies**

UV–Vis titration of L with increasing concentrations of Al<sup>3+</sup> (Figure 1).

Firstly, UV–Vis titration spectrum of L upon addition of various concentrations of  $Al^{3+}$  was carried out in ethanol and water (3:1, v/v) at room temperature. The L in the absence of  $Al^{3+}$  exhibited a relatively weak absorption band at 226nm, which was probably assignable to chromone moiety. The addition of increasing concentrations of  $Al^{3+}$  induced gradual enhancement at 226nm. At the same time, this band had a slight red-shift to 242nm. Besides, the solution of L displayed a broad band around 325nm, upon the addition of  $Al^{3+}$ , the absorbance bands at 275nm, 330nm, 435nm enhanced. These results suggested that L participated in the coordination with  $Al^{3+}$ .



**Figure 1.** The UV-Vis titration spectrum of L (50.0 $\mu$ M) with Al<sup>3+</sup> (0.0-1.3equiv) in ethanol and water (3:1, v/v).

#### **Emission studies**

#### Selectivity of L towards Al<sup>3+</sup> over other metal ions (Figure 2). A

fluorescence study was further used to determine the selectivity and sensitivity of L in the presence of various metal ions (Na<sup>+</sup>, K<sup>+</sup>, Ag<sup>+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, and Al<sup>3+</sup>). The fluorescence responses were conducted by adding 1.0equiv of Al<sup>3+</sup> and 1.0equiv other metal ions to the ethanol and water (3:1, v/v) solution of L respectively. Fascinatingly, the treatment of L with Al<sup>3+</sup>

led to a strong enhancement of the fluorescence intensity in the emission spectrum at 508nm upon excitation at 420nm. What's more, no such effect was observed when L was treated with other cations. Therefore, the sensor exhibited high selectivity for Al<sup>3+</sup> over other metal ions.



**Figure 2.** Fluorescence responses of L (50.0 $\mu$ M) in ethanol and water (3:1, v/v) with 1equiv Na<sup>+</sup>, K<sup>+</sup>, Ag<sup>+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>and Al<sup>3+</sup> ( $\lambda$ ex=420 nm).

**Competition of L towards AI^{3+} over other metal ions (Figure 3).** Competition experiments were carried out to explore the possibility of using L as a practical ion selective fluorescent sensor for  $AI^{3+}$ . For this purpose, L was treated with 1.0equiv  $AI^{3+}$  in the presence of 1.0equiv other metal ions. Relatively low interference was observed for the detection of  $AI^{3+}$  in the presence of most metal ions. L responding for  $AI^{3+}$  in the presence of Fe<sup>3+</sup> and Ni<sup>2+</sup> were relatively low but clearly detectable. In the presence of Cu<sup>2+</sup>, the fluorescence of the L-AI<sup>3+</sup> system was almost quenched, which might be due to an energy or electron transfer [35-37]. Consequently, L was shown to be a promising selective fluorescent sensor for  $AI^{3+}$  in the presence of most competing metal ions.



**Figure 3.** Relative fluorescence of L and its complexation with  $Al^{3+}$  in the presence of various metal ions in ethanol and water (3:1, v/v). Black bar: L (50.0µM) with 1.0 equiv Ag<sup>+</sup>, Ba<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Ca<sup>2+</sup>, Hg<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup>stated. Red bar: 50.0µM of L and 1.0equiv Al<sup>3+</sup> in the presence of 1.0equiv other metal ions stated ( $\lambda$ ex=420 nm).

#### Fluorescence titration experiments of L in the presence of increasing

concentrations of Al<sup>3+</sup> (Figure 4). Fluorescence titration experiments were conducted upon addition of increasing concentrations of Al<sup>3+</sup>. The free L exhibited no emission band at 508nm, and gradual enhancement in fluorescence emission intensity at 475nm and 508nm was observed with the addition of Al<sup>3+</sup>. These phenomena indicated that the L and Al<sup>3+</sup> have successfully combined. The detection limit of L for the analysis of Al<sup>3+</sup> was also calculated based on the fluorescence titration experiments. The detection limit was calculated by the following equation: detection limit= $3\sigma/k$  [38], where  $\sigma$  was the standard deviation of blank measurements, and k was the slope between fluorescence intensity versus sample concentration. As shown in **Figure.S9(a)**, it reached at  $1.82 \times 10^{-7}$ M, which was lower than the tolerable Al<sup>3+</sup> concentration in drinking water set by WHO.



**Figure 4.** Fluorescence emission titration spectra of L (50.0 $\mu$ M) upon addition of Al<sup>3+</sup> (0.0-1.8equiv) in ethanol and water (3:1, v/v) ( $\lambda$ ex=420 nm).

Effect of pH (Figure 5). In view of the importance of pH value adaptation in practical applications, we investigated the effect of pH on the fluorescence intensity at 508 nm of L. In the pH range of 5.0-8.0, the fluorescence intensity at 508 nm of L remained and relatively low interference was observed for the detection of  $AI^{3+}$ . Significantly, on moving beyond the pH range of 5.0-8.0, the fluorescence intensity at 508 nm of L- $AI^{3+}$  gradually decreased and even quenched. Therefore, these results indicated that this sensor could exist steadily and detect  $AI^{3+}$  in the pH range from 5.0 to 8.0.



**Figure 5.** Effect of pH on the fluorescence intensity at 508nm of L (50.0 $\mu$ M) in the absence and presence of 1.0equiv Al<sup>3+</sup> in ethanol and water (3:1, v/v) ( $\lambda_{ex} = 420$  nm).

#### **Binding studies**

**Binding stoichiometry between L and Al<sup>3+</sup>(Figure 6).** In order to determine the stoichiometry between L and Al<sup>3+</sup>, the method of continuous variation (Job's plot) was used [39]. During this experimental process, the total concentration of L and Al<sup>3+</sup> was kept constant at 50.0 $\mu$ M, with a continuous variable molar fraction of guest [Al<sup>3+</sup>] /([L] + [Al<sup>3+</sup>]). It can be seen that the fluorescence emission intensity at 508 nm reached maximum at the molar ratio of 0.36, establishing a 2:1 binding stoichiometry between L and Al<sup>3+</sup>. Furthermore, the ESI-MS spectrum of L and Al<sup>3+</sup> in DMF showed a peak at 829.2(m/z) that was assignable to [2L+Al<sup>3+</sup>-2H<sup>+</sup>]<sup>+</sup> (**Figure.S7**), which further gave solid evidence for the formation of a 2:1 complex between L and Al<sup>3+</sup>.



**Figure 6.** Job's plot of L with  $Al^{3+}$  in ethanol and water (3:1, v/v). The total concentration of L and  $Al^{3+}$  is 50.0  $\mu$ M ( $\lambda$ ex=420 nm).

#### Association constant between L and Al<sup>3+</sup>. As shown in Figure.S9(b), the

association constant  $K_a$  of the complex was calculated to be  $9.24 \times 10^3 \text{ M}^{-1}$  with a linear relationship by the Benesi–Hildebrand equation (Eq. (1)) [40], where  $F_{max}$ ,  $F_{min}$ , and F are fluorescence intensities of L in the presence of  $Al^{3+}$  at saturation, free L, and any intermediate  $Al^{3+}$  concentration.

(1)

$$\frac{1}{F-F_{\min}} = \frac{1}{K(F_{\max}-F_{\min})[Al^{3+}]} + \frac{1}{F_{\max}-F_{\min}}$$

Binding mode between L and  $Al^{3+}$ . <sup>1</sup>H NMR studies provided additional evidence of the interaction between L and  $Al^{3+}$ . <sup>1</sup>H NMR spectra of L were recorded in DMSO-d<sub>6</sub> upon the addition of  $Al^{3+}$ . Spectral changes were observed as shown in Figure.S6. The  $\delta$  11.27ppm signal for –OH disappeared upon the addition of  $Al^{3+}$ , which indicated that the direct involvement of the oxygen atom of the –OH group coordinate with  $Al^{3+}$ . In IR spectra (Figure.S8) ,the C=O of hydrazide frequency decreased from 1660cm<sup>-1</sup> to 1636cm<sup>-1</sup>, and the imine C=N vibration at 1602cm<sup>-1</sup> was absent in the complex. At the same time, a new frequency of 1374cm<sup>-1</sup> appeared, which was assigned to C-N stretching vibration [41-42]. These findings suggested the carbonyl oxygen atom of hydrazide and the nitrogen atom of C=N group were also in for coordinating with  $Al^{3+}$ . Besides, according to some literature, we found that when aluminum ions were involved in the coordination, the complexes always formed five or six membered rings, which were relatively stable [43-52].

Based on these results above, the proposed binding mechanism for the fluorescence response of L towards  $Al^{3+}$  was discussed. As shown in **Scheme 2**, the fluorescence emission of free L was nearly quenched and it was due to the photo induced electron transfer (PET) phenomenon that was caused by lone pair electron from Schiff-base nitrogen atom to the chromone moiety and C=N isomerization process. Nevertheless, when  $Al^{3+}$  was treated with L, two nitrogen atoms of the azomethine groups participated in the coordination with  $Al^{3+}$  and formed a 2:1 complex. As a result, the fluorescence emission of L centered at 508 nm enhanced

significantly in the presence of Al<sup>3+</sup>.

#### Application of L as solid state sensors

Inspired by the conspicuous colorimetric change of L upon addition of  $Al^{3+}$  in solution, we further tested  $Al^{3+}$  level on filter paper. For this purpose, L was adsorbed on the filter paper by immersing filter papers in the DMF solution of L (5mM) and then drying them in the air. Then the ethanol and water (3:1, v/v) solutions of various metal ions (5mM) were dropped in test strips. As shown in **Scheme 3**, the color of coated test paper changed from black to pale yellow under illumination using a 365 nm UV lamp with the addition of  $Al^{3+}$ . Such a drastic colorimetric change was attributed to the formation of L- $Al^{3+}$  complex. Therefore, this probe L could be applied for the detection of  $Al^{3+}$  in practical samples by the naked eye.



**Scheme 3:** Fluorescence color changes of L(5mM) loaded filter paper in the presence of various metal ions(5mM) under illumination using a 365 nm UV lamp.

#### Conclusion

In conclusions, we designed and synthesized a chromone derived Schiff-base ligand as an  $Al^{3+}$  fluorescent sensor based on the PET mechanism and C=N

isomerization process. This sensor had good selectivity and high sensitivity for  $Al^{3+}$  in the presence of most metal ions, the detection limit of L for sensing  $Al^{3+}$  could reach  $1.82 \times 10^{-7}$ M. Furthermore, the sensor could exist steadily and detect  $Al^{3+}$  in ethanol and water (3:1, v/v) in the pH range of 5.0–8.0. Thus, we believe that L has the ability to serve as a potential sensor for sensing  $Al^{3+}$ . This strategy may provide a general way for designing new probes to detect other environmentally and biologically relevant species.

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Figure 1. The UV-Vis titration spectrum of L (50.0 $\mu$ M) with Al<sup>3+</sup> (0.0-1.3equiv) in

ethanol and water (3:1, v/v).

**Figure 2.** Fluorescence responses of L (50.0 $\mu$ M) in ethanol and water (3:1, v/v) with 1equiv of Na<sup>+</sup>, K<sup>+</sup>, Ag<sup>+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup> and Al<sup>3+</sup> ( $\lambda$ ex=420 nm).

**Figure 3.** Relative fluorescence of L and its complexation with  $Al^{3+}$  in the presence of various metal ions in ethanol and water (3:1, v/v). Black bar: L (50.0µM) with 1.0 equiv of Ag<sup>+</sup>, Ba<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Ca<sup>2+</sup>, Hg<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup>stated. Red bar: 50.0µM of L and 1.0equiv of Al<sup>3+</sup> in the presence of 1.0equiv of other metal ions stated ( $\lambda$ ex=420 nm).

**Figure 4.** Fluorescence emission titrations spectrum of L (50.0 $\mu$ M) upon addition of Al<sup>3+</sup> (0.0-1.8equiv) in ethanol and water (3:1, v/v) ( $\lambda$ ex=420 nm).

**Figure 5.** Effect of **pH** on the fluorescence intensity at 508nm of L (50.0 $\mu$ M) in the absence and presence of 1.0equiv Al<sup>3+</sup> in ethanol and water (3:1, v/v) ( $\lambda$ ex=420 nm). **Figure 6.** Job's plot of L with Al<sup>3+</sup> in ethanol and water (3:1, v/v). The total concentration of L and Al<sup>3+</sup> is 50.0 $\mu$ M ( $\lambda$ ex=420 nm).

Scheme 1. The synthetic route of 6-ethoxychomone-3 carbaldehyde-(3-hydroxy-2-naphthalene acyl) hydrazone (L).

Scheme 2. The proposed sensing mechanism of L and  $Al^{3+}$ .

**Scheme 3:** Fluorescence color changes of L(5mM) loaded filter paper in the presence of various metal ions(5mM) under illumination using a 365 nm UV lamp.



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Scheme 1. The synthetic route of 6-ethoxychromone-3-carbaldehyde-(3-hydroxy-2-naphthalene acyl) hydrazone (L).



**Scheme** 2. The proposed sensing mechanism of L and  $Al^{3+}$ .



**Scheme 3:** Fluorescence color changes of probe L(5mM) loaded filter paper in the presence of various metal ions(5mM) under illumination using a 365 nm UV lamp.



- We designed and synthesized a new Off-on fluorescent sensor for the detection of Al<sup>3+</sup>, 6-ethoxychromone-3-carbaldehyde-(3-hydroxy-2-naphthalene acyl) hydrazone (L).
- The sensor showed good selectivity and high sensitivity for the detection of  $Al^{3+}$ in ethanol and water (3:1, v/v), and the detection limit of L for  $Al^{3+}$  was as low as  $1.82 \times 10^{-7}$ M.
- With the fluorescence titration experiments and the ESI-MS spectrum data, we reached the conclusion that the binding ratio between L and Al<sup>3+</sup> was 2:1.

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• The yield of L can be reached 95.4%.