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# Synthesis and properties of oil-soluble butyl crystal violet lactone

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**Abstract** A novel compound of butyl crystal violet lactone (BCVL) has been prepared by oxidizing leuco butyl crystal violet lactone (LBCVL), which was obtained by the mixture of *N,N*-dibutylaniline, *p*-(dibutylamino) benzaldehyde and methyl-*m*-(dibutylamino) benzoate. The structure of BCVL was characterized by <sup>1</sup>H- nuclear magnetic resonance (NMR), infrared (IR), and mass spectrometry (MS). The color of BCVL can change reversibly in some acid or alkali solvents. The result of the dissolution experiment showed that solubility of BCVL in organic solvent was improved compared with crystal violet lactone (CVL).

**Keywords** leuco butyl crystal violet lactone, oil-soluble, butyl crystal violet lactone

## 1 Introduction

A thermochromic compound changes color when heated and reverts to its original color upon cooling. This phenomenon is known as the thermochromic property [1–2]. Organic reversible thermochromic complexes are increasingly gaining importance in recent years in the research field and its application in textiles and smart coating. Especially, organic complexes with a leuco dye (electron donor), a weak acid (electron acceptor), and a solvent are commonly used in consumer applications because the temperature at which they change color can be presented within the living-environment temperature range. In the past decade, many complexes from crystal violet lactone (CVL) were reported as three-component thermochromic dye mixtures [3–11]. Triphenylmethane dye is one of the most widely used organic color-changing dyes, and CVL is also a familiar one. Crystal violet lactone has been used to prepare microcapsule,

pressure-sensitive, heat-sensitive, photosensitive, and other recording materials [12–17]. This color-developing leuco dye can be used in recording materials in combination with other special compounds, such as carbazoly methane derivatives, to produce color images of excellent light resistance, water resistance or plasticizer resistance.

However, CVL cannot dissolve well in long chain aliphatic hydrocarbons, which confines its application in some fields. To improve the solubility of the dye in organic solvent, a new structure compound, butyl crystal violet lactone (BCVL), was prepared by modifying the functional group of CVL.

The present work describes a novel compound of BCVL that was obtained by the mixture of *N,N*-dibutylaniline, *p*-(dibutylamino) benzaldehyde and methyl *m*-(dibutylamino) benzoate. The BCVL can change color reversibly in some acid or alkali solvents. The result of the experiment shows that solubility of BCVL in organic solvent has been improved compared with CVL.

## 2 Experimental

Butyl crystal violet lactone was oxidized by hydrogen peroxide solution in the alkaline system and was synthesized as shown in Scheme 1.

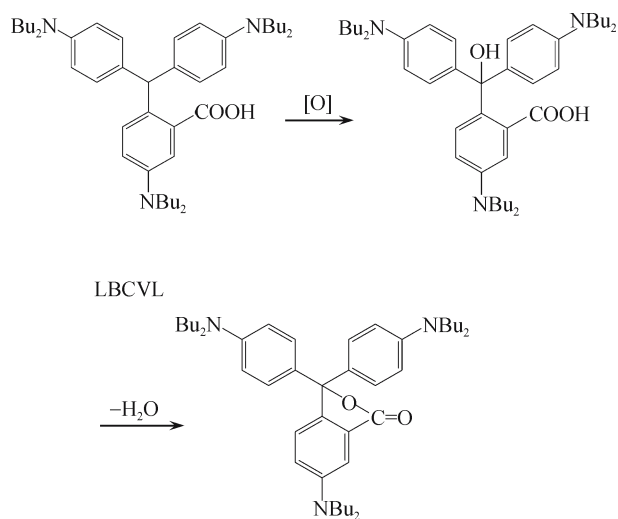
### 2.1 Materials and measurements

Aniline, bromobutane, methyl alcohol, dimethyl formamide (DMF), dimethyl sulfocide (DMSO), hydrogen peroxide, phosphorus oxychloride, potassium iodide, and hydroxyurea were dried and purified in route. *N,N*-dibutylaniline, *p*-(dibutylamino) benzaldehyde and methyl *m*-(dibutylamino) benzoate were prepared by others in our lab [18].

<sup>1</sup>H-nuclear magnetic resonance (NMR) analyses were performed on a BRUKER DMX 500 spectrometer. Fourier transform infrared (FT-IR) spectra ranging from 400 to 4 000 cm<sup>-1</sup> were obtained using a Nicolet Magna-IR 550-II FT-IR spectroscope. A Netzsch DSC 204 differential scanning calorimeter was used for the assessment of thermal transitions. Heating rate was 10°C/min. Element analyses

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**Scheme 1** Scheme of synthesis BCVL

were obtained on GmbH Vario EL III element analyses instruments. Liquid chromatographic-mass spectrometry (LC-MS) analyses were performed on Voyager LC-MS instruments. High performance liquid chromatographic (HPLC) analyses were performed on Agilent 1100 HPLC instruments.

## 2.2 Synthesis of LBCVL

Hydrochloric acid (7.5 mL) and DMSO (10 mL) were mixed. *N,N*-dibutylaniline (5.64 g), *p*-(dibutylamino)benzaldehyde (5.83 g), methyl *m*-(dibutylamino) benzoate butyl aniline (6.58 g) and hydroxyurea (1.50 g) were added. Then the solution was heated to 70°C and kept for 7 h. The color became deep blue. After being cooled down to room temperature, the solution was adjusted to pH = 5 by adding a saturated solution of sodium carbonate. Then the organic compound was extracted by petroleum ether and concentrated by distillation (250°C/800 Pa). The obtained brown liquid was further purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 35/1), and the content of LBCVL analyzed by HPLC was in 94.27%.

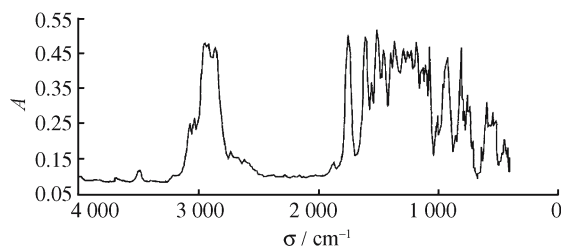
## 2.3 Synthesis of BCVL

Leuco butyl crystal violet lactone (LBCVL) (6.83 g, 0.01 mol) was dissolved in DMSO (150 mL). Then the reaction was heated to 100°C. NaOH (10 mol/L, 10 mL) and ammonium molybdate (0.0008 mol) were added to the reaction. H<sub>2</sub>O<sub>2</sub> (10%, 10 mL) was added dropwise into the above stirred solution. Afterwards, the reaction was maintained at reflux for 1 h. The operation of H<sub>2</sub>O<sub>2</sub> was repeated five times. After being cooled down to room temperature, the reaction mixture was adjusted to pH = 3–5 by dilute hydrochloric acid. Then the organic was extracted by ether and concentrated by distillation (250°C/800 Pa). The obtained brown liquid was further purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 1/0, 50/1, 40/1, 30/1, 20/1), and the content of BCVL analyzed by HPLC was in 93.80%.

## 3 Results and discussion

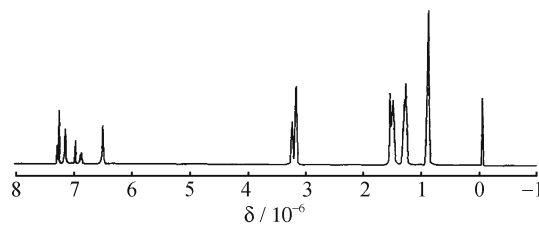
### 3.1 Characterization of BCVL

Figure 1 shows the IR spectra of BCVL. The absorption bands centered at 3 079, 3 046 cm<sup>-1</sup> are due to the vibration of Ph—H and that at 2 965, 2 872 cm<sup>-1</sup> are due to the vibration of C—H. The absorption band centered at 1 767 cm<sup>-1</sup> is due to the carbonyl stretches and that at 1 691–1 565 cm<sup>-1</sup> is due to the phenyl ring vibration.



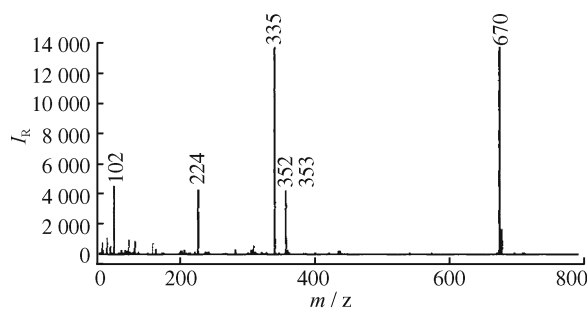
**Fig. 1** IR spectra of BCVL

Figure 2 shows the <sup>1</sup>H-NMR spectrum of BCVL. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) (ppm): 0.91–0.97 [t, 18H, —CH<sub>3</sub>], 1.28–1.39 [m, 12H, —CH<sub>2</sub>—], 1.51–1.58 [m, 12H, —CH<sub>2</sub>—], 3.20–3.23 [t, 8H, Ph—N(CH<sub>2</sub>)<sub>2</sub>—], 3.27–3.30 [t, 8H, Ph—N(CH<sub>2</sub>)<sub>2</sub>—], 6.50–7.30 [s, 11H, Ph—H].



**Fig. 2** <sup>1</sup>H-NMR spectrum of BCVL

Figure 3 shows the LC-MS spectrum of BCVL. It could be seen from Fig. 3 that the measured datum (670) was close to the theoretical calculation (667).



**Fig. 3** LC-MS spectrum of BCVL

Figure 4 shows the DSC spectrum of BCVL. It could be seen from Fig. 4 that one endothermic peak at 0°C was found on the DSC heating curve of BCVL. It was the melting point of BCVL.

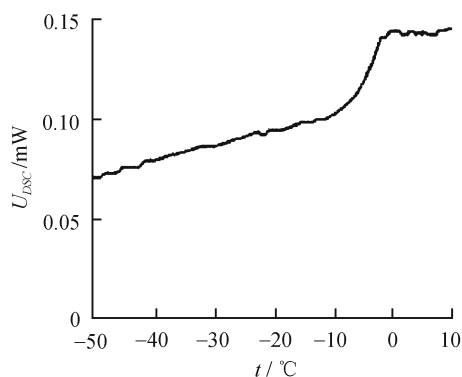


Fig. 4 DSC spectrum of BCVL

The results of elemental analyses are shown in Table 1. The results demonstrated that the measured data were close to the theoretical calculation.

Table 1 Elemental analysis of BCVL

	w(N)/%	w(C)/%	w(H)/%
BCVL	6.276	79.53	9.865
Theory	6.297	79.16	9.745

### 3.2 The quantity of H<sub>2</sub>O<sub>2</sub>

Figure 5 shows the relationship between  $n(\text{H}_2\text{O}_2)$  and BCVL. It could be seen from Fig. 5 that when the mole ratio of H<sub>2</sub>O<sub>2</sub>/LBCVL is up to 3, the concentration of BCVL no longer increases. This indicates that the reaction is complete under this condition. Therefore, the mole ratio of H<sub>2</sub>O<sub>2</sub>/LB-CVL = 3:1 is the proper condition.

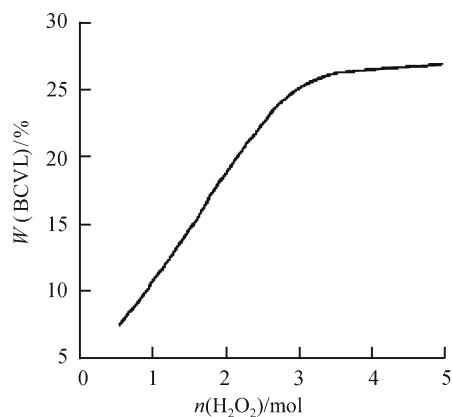


Fig. 5 The relationship curve of  $n(\text{H}_2\text{O}_2)$  and  $W(\text{BCVL})$

### 3.3 Dissolvability of BCVL

The dissolvability of BCVL and CVL (offered by Jikang Biochemistry Technological Co., Ltd. in Shanghai) were tested. The results are shown in Table 2.

Table 2 Comparison of dissolvability between CVL and BCVL (at room temperature)

Solvent	H <sub>2</sub> O	Ethanol	Acetone	Toluene	Petroleum ether	Ether	Cyclo-hexane	Solvent oil
CVL	-	++	+++	++	+	+	+	+
BCVL	-	+++	+++	+++	+++	+++	+++	+++

- undissolved, + little dissolved, ++ dissolved, +++ diffuent

As shown in Table 2, both CVL and BCVL were dissolved in organic solvents such as ethanol, acetone, toluene, and undissolved in H<sub>2</sub>O at room temperature. CVL is undissolved in oil, petroleum ether, cyclohexane, and nonpolar organic solvents; however, BCVL is dissolved in these kinds of organic solvents. The solubility of BCVL in organic solvent has been improved evidently compared with CVL.

### 3.4 Performance of color change

Figure 6 shows the ultraviolet (UV)-visible absorption spectra of BCVL using isopropanol as solution. It could be seen from Fig. 6 that the absorption peak of a solution of BCVL in isopropanol was below 450 nm. The absorption peak of BCVL solution in a mixture of acid and isopropanol appeared not only at below 450 nm, but also at 550–650 nm. The color of BCVL changed to blue in acid.

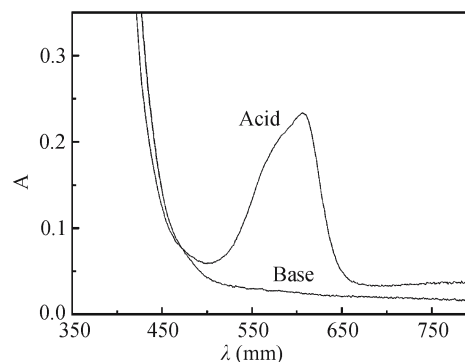


Fig. 6 UV-visible absorption spectra in isopropanol solution

The color changing mechanism of CVL has been extensively studied. The color changing mechanism of BCVL is shown in Scheme 2.

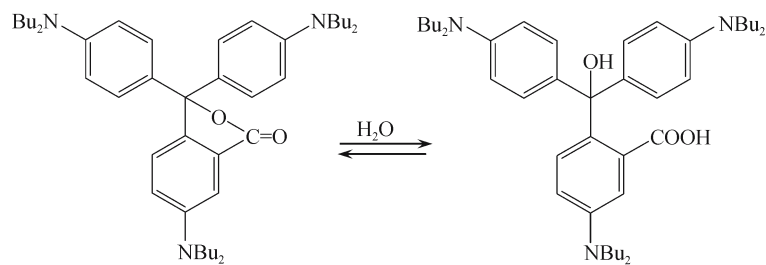
#### a) The reversible dependence of color on pH

In general, BCVL is brown in color. It turned to blue when acid was added, and reverted to brown when alkali (some inorganic and organic alkali such as ethylenediamine) was added. These processes were reversible. The mechanism of changing color is similar to CVL.

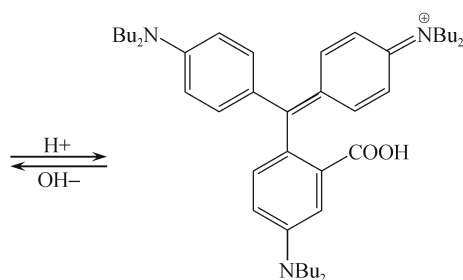
#### b) The reversible color change on temperature

The color of BCVL changed to blue when acetic acid was added into the BCVL and after being cooled down to room temperature.

Acetic acid volatilized when the temperature exceeded its boiling point. The solution became neutral and the quinone turned to triphenylmethane. The color of BCVL solution changed from blue to brown. It reverted to quinone showing blue when it was cooled and acid was added. Therefore, BCVL can be used as a reversible heat-sensitive discolorable material.



Interior ester structure (brown)



Quinone conjugation structure (blue)

**Scheme 2** The mechanism of changing color of BCVL

## 4 Conclusions

The melting point of BCVL is 0°C. The mole ratio of H<sub>2</sub>O<sub>2</sub> / BCVL = 3/1 is the proper condition to prepare BCVL. The solubility of BCVL in organic solvent has been improved compared with CVL. The BCVL can change color reversibly in some acid or alkali solvents.

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