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# Synthesis of Novel Morpholine Appended Crystal violet lactone Derivatives and an Investigation of their Thermochromic Behavior

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**Abstract** In the present study, three morpholine substituted crystal violet lactone (CVL) have been synthesized to monitor the thermochromic property. This work is explaining the role of substituent on the lactone ring. The methyl substituents induced greater chromic effects than the chloro substituents. Furthermore, the three-component mixtures that contained CVL, bisphenol-A, and methyl stearate were used to analyse the thermochromic effect of the CVLs as bulk samples with various temperature. The thermochromic properties of the CVLs were evaluated using solid-state UV-Vis and FT-IR spectroscopic techniques. Finally, one of the synthesized CVL has been successfully converted into the form of a test paper similar to pH paper for use as thermal indicators.

**Keywords** *CVL, leuco dyes, morpholine, substituent effect, thermal indicator*

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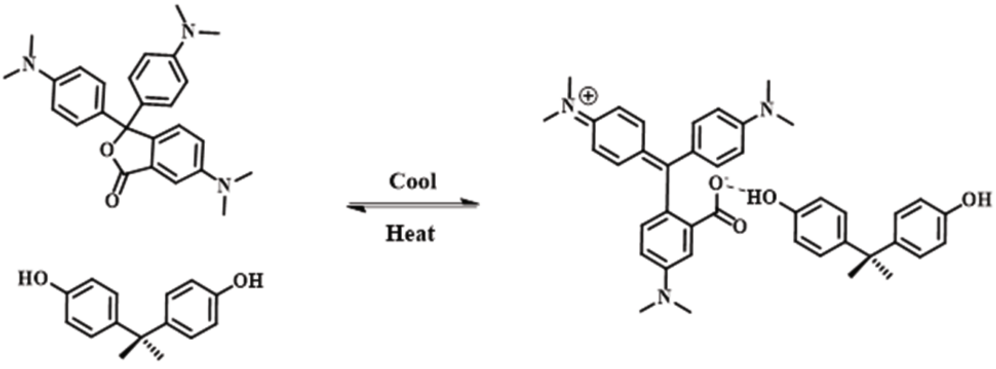
## 1. Introduction

Currently, dyes have great attention due to their application in various fields such as thermochromic materials, luminescent and other optical storage materials[1-4]. Already, many examples were available for thermochromic materials such as crystal violet lactone (CVL), fluorans, spiropyrans, metal-complexes and polydiacetylnes[5-8]. In the aforementioned materials, CVLs have significant interest due to their very good photo-physical properties in response to heating and cooling process. Up to now, CVLs used as a dye for thermochromic system[9-11] as well as pressure recording materials[12-14]. In addition, numerous amount of xanthene and leuco dyes were used as thermochromic materials via three component formulations[15,16]. These three component mixture consisting with color producer (leuco dyes), color developer (proton donor), and low melting solvent[17]. The color formation in solid state is due to proton transfer between the weak acid and leuco dye in low temperature, resulting a formation of ring-opened structure in active dye.

In these three components, low melting co-solvents have vital role, because it controls the association between color former and color developer on its own melting point. Thus, the creation of the thermochromic properties is mainly depends on the design of the three component systems. To prepare thermochromic system, the three components solid mixtures were heated until the color former and color developer was dissolved completely in the low melting solvents and to get the homogeneous liquid. Henceforth, the homogeneous three components liquid mixture was slowly cool down and the color of the cooled mixture was turned to visible color. However, these three components system produce high reversibility with heating and cooling process (Scheme 1)[18-21]. Because the interactions between dye and proton donor must be alter in the phase between the



**Scheme 1.** Thermochromic response of CVL–bisphenol A system.

colored solid and colorless liquid phase depend on the temperature[21, 22].

Based on the literature survey, the CVL act as a potential candidate in pressure and thermo-sensitive recording materials[23-25]. In such a manner, Ondrej Panak et al. have developed the relation between color and structural changes in thermochromic systems comprising crystal violet lactone, bisphenol A, and tetradecanol[26]. In recent years, our research group studied the synthesis of novel tert-butyl substituted fluorans and an investigation of their thermochromic behavior[27]. Similarly, in this present endeavor, we synthesized three morpholine substituted CVL, which have different substituents on the lactone ring, such as electron donating methyl, electron withdrawing chloro and unsubstituted lactone.

Furthermore, we discuss the thermochromic properties of the CVL (CVL1-CVL3) with respect to electronic effects. Eventually, we discussed the thermochromic properties of CVL1-CVL3 in the solid state and subsequently achieved paper strip as thermal indicator.

## 2. Experimental Section

### 2.1 Equipment and reagents

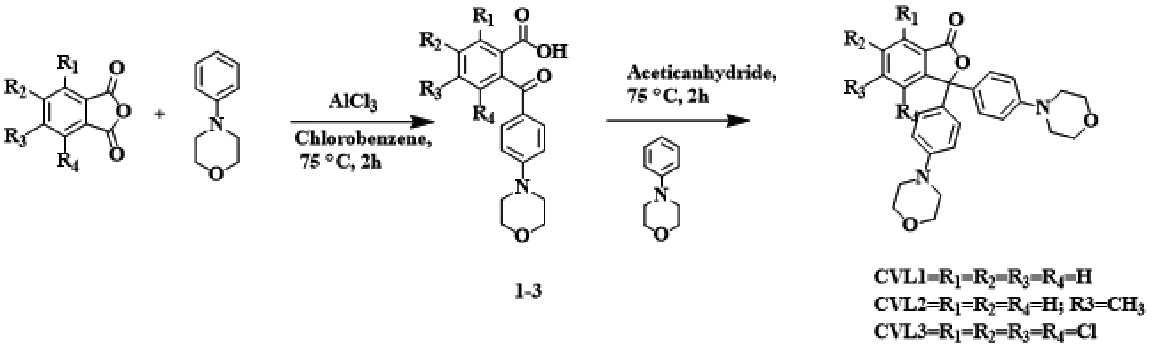
All chemicals and reagents were purchased from either Aldrich or TCI chemicals and were used as such. NMR spectra were recorded on a Bruker Avance 300 MHz instrument ($^1$H NMR 300MHz) with tetramethylsilane as an internal reference. Flash column chromatography was used for purify new compounds by using 230-400 mesh silica gel. Solid state UV-Vis absorption spectra of the new CVLs in methyl stearate and bisphenol-A were performed on a Shimadzu Solid Spec-3700. FT-IR spectra were recorded using a Perkin Elmer Spectrum One spectrophotometer equipped. The intermediates(1-3) and CVLs (CVL1-CVL3) for this endeavor were synthesized as depicted in Scheme 2.

### 2.2. General method for the preparation of intermediates(1-3)

$AlCl_3$(2.0 equiv) was added portion wise in to the stirred solution of 4-phenylmorpholine(1.0 equiv) and substituted phthalic anhydride(1.0 equiv) in chlorobenzene under $N_2$ and the reaction mixture was heated at 60 °C for 2h then allowed to RT. The resulting reaction mass was diluted with distilled water, and acidified with 1N HCl at 0°C, and stirred the reaction mixture for 0.5h at ambient temperature. Then the solid substance filtered through the filter paper. The crude half-white solid was obtained by recrystallization with water and methanol mixture.

#### 2.2.1 2-(4-morpholinobenzoyl)benzoic acid (1)

To acquire the pure intermediate 1, the crude material was purified by column chromatography by using 20% ethylacetate in petroleum ether. (White solid, Yield=60.0 %)



**Scheme 2.** Synthetic route for preparation of CVL1–CVL3.

### 2.2.2 3-methyl-2-(4-morpholinobenzoyl)benzoic acid (2)

To acquire the pure intermediate 2, the crude material was purified by column chromatography by using 15% ethylacetate in petroleum ether. (White solid, Yield=69.0%)

### 2.2.3 2,3,4,5-tetrachloro-6-(4-morpholinobenzoyl)benzoic acid (3)

To acquire the pure intermediate 3, the crude material was purified by column chromatography by using 30% ethylacetate in petroleum ether. (Pale yellow solid, Yield=45.0%)

### 2.3 General method for the preparation of CVL1-CVL3

A solution of intermediates(1-3) and 4-phenylmorpholine in aceticanhydride was heated at 90°C for 2h and cooled to ambient temperature then 20mL of 30% NaOH was slowly added in drops to the reaction mixture. Further the reaction mixture was stirred at room temperature for 1h. Finally, the obtained crude solid was filtered and purified by column chromatography with gradual enhancement of ethylacetate in petroleum ether to obtain a pure product.

### 2.3.1 3,3-bis(4-morpholinophenyl)isobenzofuran-1(3H)-one (CVL1)

$^1$H NMR (DMSO-D6, 300MHz), δ(ppm): 3.05(t,8H,J=9.0Hz), 3.72(m,8H), 6.95(d,4H,J=9.0Hz), 7.15(d,4H,J=7.8Hz), 7.65(t,1H,J=7.2Hz), 7.76(m,3H)(Yield=65.0%).

### 2.3.2 5-methyl-3,3-bis(4-morpholinophenyl)isobenzofuran-1(3H)-one (CVL2)

$^1$H NMR (DMSO-D6, 300MHz), δ(ppm): 2.35(s, 3H), 3.08(t, 8H, J =7.8 Hz), 3.70(t, J =4.8 Hz 8H), 6.92(m, 4H), 7.12(m, 4H), 7.52(m, 2H, J = 7.2 Hz), 7.76(m, 1H)(Yield = 68.0%).

### 2.3.3 4,5,6,7-tetrachloro-3,3-bis(4-morpholinophenyl)isobenzofuran-1(3H)-one (CVL3)

$^1$H NMR (DMSO-D6, 300MHz), δ(ppm): 3.08(t, 8H, J = 9.0Hz), 3.82(t, 8H, J = 5.1Hz), 7.12(d, 4H, J = 9.0Hz), 7.36(d, 4H, J = 9.2Hz) (Yield = 55.0%).

## 3. Results and Discussion

### 3.1 Color properties in protic and aprotic solvents

When dissolved in aprotic solvent such as toluene, compound CVL1-CVL3 does not exhibit any significant color changes. This result reveals that in aprotic solvent, these compounds hold their colorless lactone form. However, when dissolving the compound CVL1-CVL3 in protic solvent (acetic acid), the color of the solution becomes deep violet color. This is mainly due to the formation of zwitterions of the CVL motifs(Figure 1).

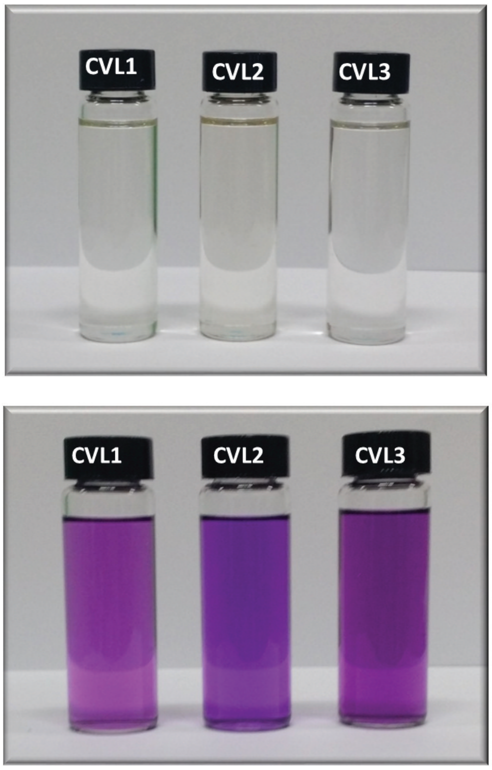


**Figure 1.** The color of CVL1–CVL3 in toluene (Top) and acetic acid (bottom).

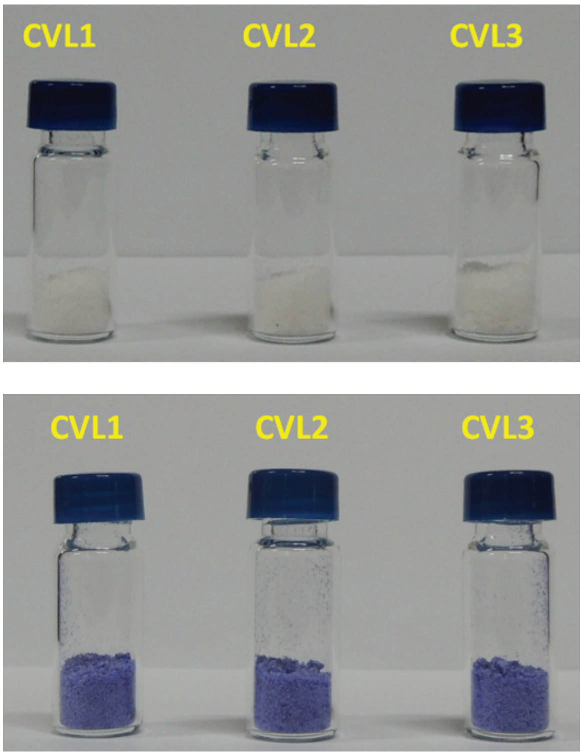


**Figure 3.** Solid state color change of CVL1–CVL3 (at warm (Top) and cool (Bottom)) with bisphenol–A and methylstearate.

### 3.2 UV-Vis absorption spectroscopic studies

To predict the electronic effect on lactone ring, the electronic spectra of CVL1-CVL3 were recorded in acetic acid displayed an intense broad peak around 550-570 nm. As shown in Figure 2, the unsubstituted lactone (CVL1) and methyl substituted lactone (CVL2) have relatively higher λmax values. While in the case of chloro substituted lactone (CVL3), λmax values is shorter. The reason for this electronic effect may be due to the n-π* transition in CVL1 and CVL2 is relatively easier than that of CVL3. This result reveals that the nature of the substituent present on the lactone has a significant role in the solution state.

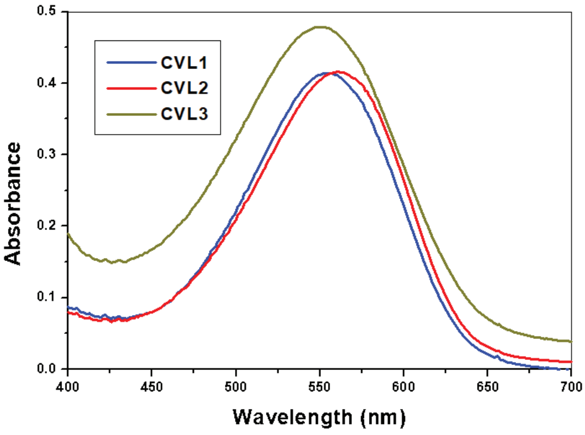


**Figure 2.** UV–Vis absorption spectra of (CVL1–CVL3) in acetic acid.

### 3.3 Thermochromic properties of CVL1-CVL3 in the solid state

To check the solid state thermochromic property of CVLs, three component composites are prepared as mentioned below: the leuco dye(5 wt.%, CVL1-CVL3) and acid activator(2.5 wt.%, bisphenol-A) were mixed in 92.5 wt.% of methylstearate at 90°C. As shown in Figure 3, these three component systems are dark violet at low temperature(below 15°C), but they turned to colorless when warmed(more than 24°C). The result reveals that ring opening of CVL system is more favored when the three components system is at cooled condition, which is due to the intermolecular

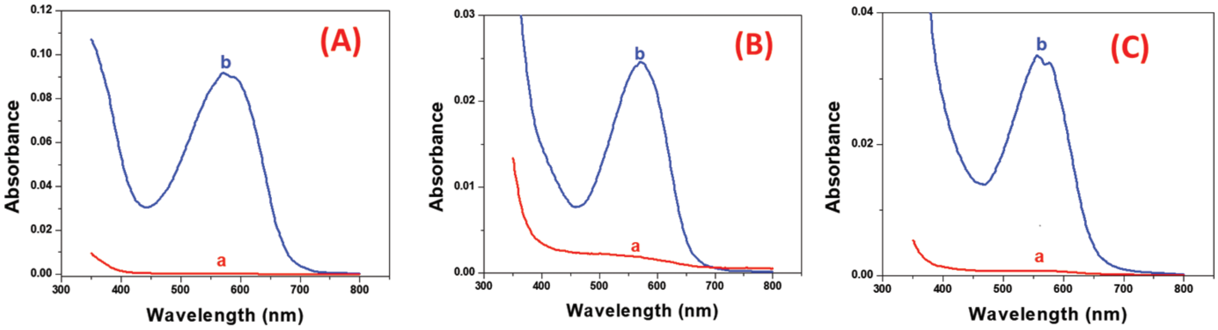


**Figure 4.** Solid state UV–Vis absorption spectra of (A) CVL1, (B) CVL2 and (C) CVL3 on (a) heating and (b) cooling.

interaction between bisphenol and lactone ring. In general, CVL1-CVL3 alone is colorless due to the presence of sp3 hybrid orbital at central carbon atom in the lactone unit. While, lactone interacts with bisphenol-A, the sp3 hybrid orbital gets transformed to sp2 in central carbon atom, as a result the conjugation gets increased therefore the redshift was observed in the electronic spectra of CVL1-CVL3 [5].

### 3.4 Solid state UV-Vis absorption studies

Solid state UV-Vis absorption spectroscopic techniques were performed to get insight about the electronic structures of three component system. The results of solid state UV-Vis study are in line with the results obtained in solution state (Figure 4).

The solid colorless three components leuco dyes (CVL1-CVL3) does not produce any significant peak at 40°C, whereas, when it was cooled to RT, these systems exhibited two absorption peaks at approximately 550 nm. This is in line with our perception, ring-opening of the lactone systems obtained by the association of lactone ring and phenolic OH at low temperature and consequently produce the violet - color[18-20, 29].

### 3.5 FT-IR spectroscopic studies

To prove the ring opening mechanism of CVL1-CVL3, FT-IR spectral study was carried out for CVLs. As depicted in Figure 5, the C=O stretching frequency of CVL1 appeared at 1738 cm$^{-1}$ for the colorless sample, whereas the cooled violet color sample, the peak corresponding to ketone was shifted to 1730 cm$^{-1}$ [27,29,30]. Similarly, CVL2 and CVL3 also produce the same effect on ketone peak. This result reveals that the decrease

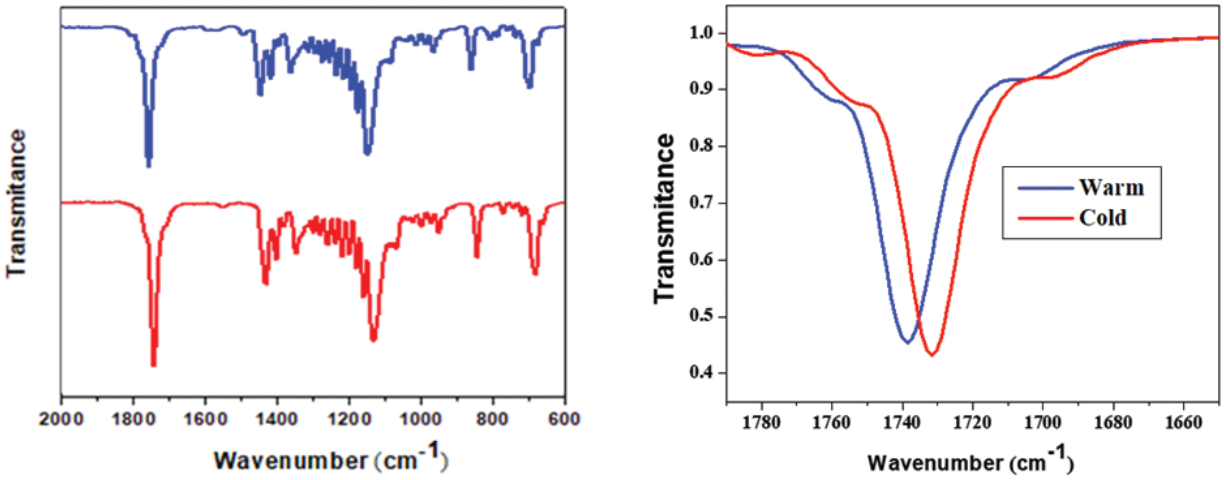


**Figure 5.** FT–IR spectra of CVL1 at heat (40℃) and cool (24℃).

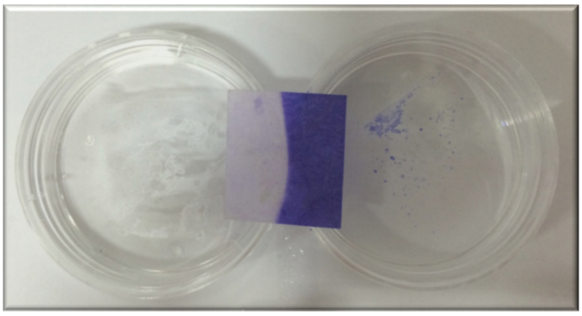


**Figure 6.** Color change of CVL1 coated thermal indicator paper at 20℃ and 40℃.

in the frequency of the C=O stretch in the cooling state is due to the lactone ring opening, resulting in the formation of carboxylate group which can easily be protonated[28,30].

### 3.6 Practical application

To further investigate the use of CVL1 under investigation, it is vital to get the product for practical or any real application. We prepared the filter paper strip as real time thermal indicator. The coloring or coating three component system was prepared by the following procedure: mixture of 5 wt.% of CVL1, 2.5wt.% of bisphenol-A and 92.5wt.% of methylstearate was heated at 90 °C until get clear solution. The filter paper was dipped in to the aforementioned hot solution and cooled to room temperature. As shown in Figure 6, a different temperature environment was applied to the filter paper strip. Depending on the temperature, the color of the filter paper changed from a violet to colorless and vice-versa.

## 4. Conclusion

In conclusion, this present endeavor, we described the role of the substituent on new CVLs with a morpholine ring and demonstrated the function of substituent on lactone ring in acidic medium. The substituent effect has also been reflecting in solid state as like solution state. The color change of CVL1 with bisphenol-A in methylstearate has been demonstrated in the form of a thin film on test paper, which can be used as a thermal indicator in real time monitoring.

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