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Combinatorial Approach for the Rapid Determination of Thermochromic Behavior of Binary and Ternary Cholesteric Liquid Crystalline Mixtures

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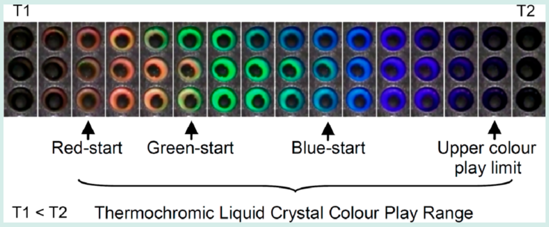
ABSTRACT: A combinatorial approach was developed for the rapid determination of thermochromic behavior of a large number of binary and ternary sterol based thermochromic liquid crystalline formulations. A binary mixture containing cholesteryl oleyl carbonate and cholesteryl nonanoate, and ternary mixtures also containing a third component, either cholesteryl oleate, cholesteryl benzoate, cholesteryl 2,4-dichlorobenzoate or cholesteryl propionate, were formulated via solvent deposition into a black Teflon coated aluminum 96 well plate. The temperature of the well plate was then varied, and the color appearance of the deposited mixture in each well was recorded. This approach allowed expedient examination of the thermochromic behavior for a large range of liquid crystal formulations. The accuracy of the rapid combinatorial technique was validated on selected thermochromic liquid crystal mixture compositions by comparing well thermochromic output with that observed using UV−vis spectroscopy on material produced in gram quantities.



KEYWORDS: *thermochromic, liquid crystal, cholesteric, formulation, binary, ternary, composition, combinatorial*

INTRODUCTION

Thermochromic liquid crystalline (TLC) materials have been widely studied and reported.[1−6] The ready tuneability, multiple color transitions and high temperature accuracy of these systems has highlighted their potential use in precision thermal mapping applications in the medical, industrial and engineering fields.[7−12] Molecules that are rigid and rod-like in shape, and chiral in nature, can form the cholesteric (chiral nematic) phase, across a defined temperature range. The cholesteric phase lies typically between a smectic and isotropic phase. The cholesteric phase is closely related to the nematic phase, in which nonchiral rod-like molecules align directionally with each other while in the liquid state due to their anisotropy.[13] The term "director" describes the long axis of the molecule. In the cholesteric phase, there is a gradual twisting of the director field through the material because of the chirality of the molecules present. This helical arrangement of molecules provides the material with useful optical properties, selectively reflecting incident light in a manner analogous to the Bragg reflection of light from a layered solid.[6] Incident light normal to the director field and circularly polarized with the same sense as the helix will be reflected according to the formula[14]

$$\lambda = nP$$

where λ is the wavelength of the selectively reflected light, n is the refractive index, and P is the pitch length, which describes the distance along the helical axis where a 360° rotation of the director field occurs. Wavelengths which are not selectively reflected are transmitted through the material. If the reflected light is in the visible region of the spectrum, the material will appear colored. Following the Bragg reflection mechanism, there is also an angular dependence on the color appearance of the material.[15] Cholesteric liquid crystals are best viewed against nonreflecting black backgrounds for optimal visualization of color.[7] This ensures that all transmitted light is absorbed and not reflected back through the material.

In a thermochromic liquid crystal there is a temperature dependency on the pitch length, where an untwisting of the helical structure (and a resultant increase in pitch length) occurs with decreasing temperature in the vicinity of the smectic-A transition.[16] In the smectic-A phase, the pitch is infinitely long.[17] This pretransitional effect results in the color of the TLC shifting from the blue end of the visible spectrum through to the red with a decrease in temperature toward the phase transition point. The reverse behavior occurs as the temperature is increased through the same range, with eventual loss of color at higher temperatures as the reflected light passes outside the visible range, and the system transitions into the isotropic phase. The color change behavior is nonlinear, with dP/dT increasing with a decrease in temperature toward the cholesteric to smectic-A transition temperature. This results in a more rapid shift in color with temperature at the red end of the visible spectrum compared to the blue.

There are a number of parameters which can be used to describe the thermochromic behavior of a TLC. The "red-

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start", "green-start", and "blue-start" temperatures are defined as the temperatures at which each of these colors are first observed as the TLC is warmed through its working temperature range. The "bandwidth" of a TLC is defined as the blue-start minus the red-start temperature.[7] The "color play" of a liquid crystal is the full temperature interval across which it appears colored. The temperature of the smectic-A to cholesteric transition determines the lower temperature limit at which thermochromism can commence, while the temperature range of the color play depends on the intrinsic cholesteric pitch length and the details of the pretransitional effects which lengthen the pitch,[6] including the helical twisting power of the mixture.[18]

Both cholesterol based and nonsterol molecules can form the cholesteric phase. This paper assesses TLC mixtures consisting of sterol based molecules. To date, a large amount of information has been published in literature regarding the phase transition temperatures and structure−property relationships of pure cholesterol based liquid crystalline compounds.[19−22] Although pure liquid crystal compounds can exhibit thermochromic behavior on their own, the behavior is typically limited to discrete and narrow temperature ranges.[3] Thus, for most applications, two or more compounds are combined together to form a mixture, where the final color play behavior can be finely tuned. Currently, TLCs can be formulated to operate with red-start temperatures ranging between −30 and 150 °C, with bandwidths between 1 and 50 °C.[23]

Previous studies have explored the transitional and color play behavior of simple binary or ternary cholesteric mixtures.[24−38] However, the disparate nature of the information and the lack of extensive experimental trials on how incremental compositional changes within mixtures containing two or more components can affect the overall thermochromic behavior of those mixtures led to further investigation of this relationship. Ultimately, the identification of compositions appropriate for use as thermochromics across specific and defined temperatures ranges has been achieved.

This paper presents a technique developed for the rapid assessment of thermochromic behavior of a number of binary and ternary TLC mixtures consisting of the following cholesterol derivatives: cholesteryl oleyl carbonate (COC), cholesteryl nonanoate (CN), cholesteryl oleate (CO), cholesteryl benzoate (CB), cholesteryl 2,4-dichlorobenzoate (CD), and cholesteryl propionate (CP) (Figure 1). These compounds were selected because they have been extensively used for the formulation of cholesterol based TLC mixtures, especially the COC/CN combination. They also represent a variety of cholesterol derivations, transition through the cholesteric phase at different temperatures, are commercially available and less expensive than their nonsterol counterparts.

This work was carried out to provide high quantity observational data regarding the thermochromic behavior of a large number of TLC mixtures. The rapid assessment combinatorial technique was validated for a small range of mixtures through comparison with UV−vis spectroscopic analysis.

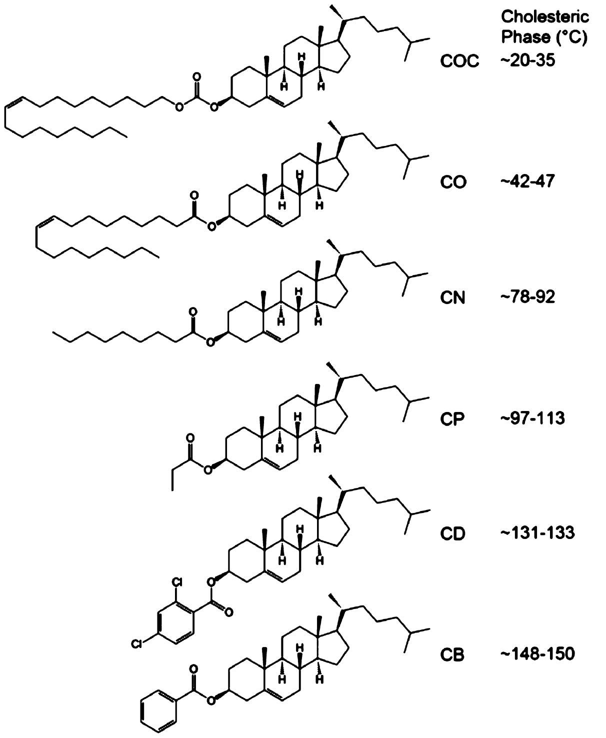
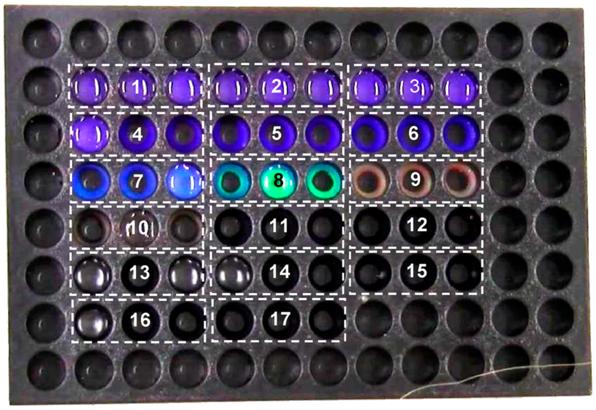


Figure 1. The six cholesterol derivatives explored and their cholesteric phase temperature ranges.[19,39−41].



Triplet no.	1	2	3	4	5	6	7	8	9	...	17
wt% COC	80	75	70	65	60	55	50	45	40	...	0
wt% CN	0	5	10	15	20	25	30	35	40	...	80
wt% CD	20	20	20	20	20	20	20	20	20	...	20

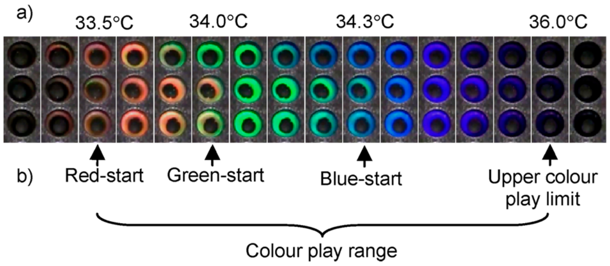


Figure 2. (a) Fabricated well plate at 34.3 °C with deposited ternary TLC mixtures comprised of COC, CN, and CD. (b) 50 wt % COC and 50 wt % CN deposited in triplicate, transitioning through its color play range.

■ RESULTS AND DISCUSSION

Binary and ternary liquid crystalline mixtures were deposited into a specialized well plate, and visually characterized under the conditions described in the Experimental Procedures. Figure 2a shows a well plate containing deposited ternary mixtures (20 mg in each well) at a recorded average temperature of 34.3 °C. This illustrative example clearly

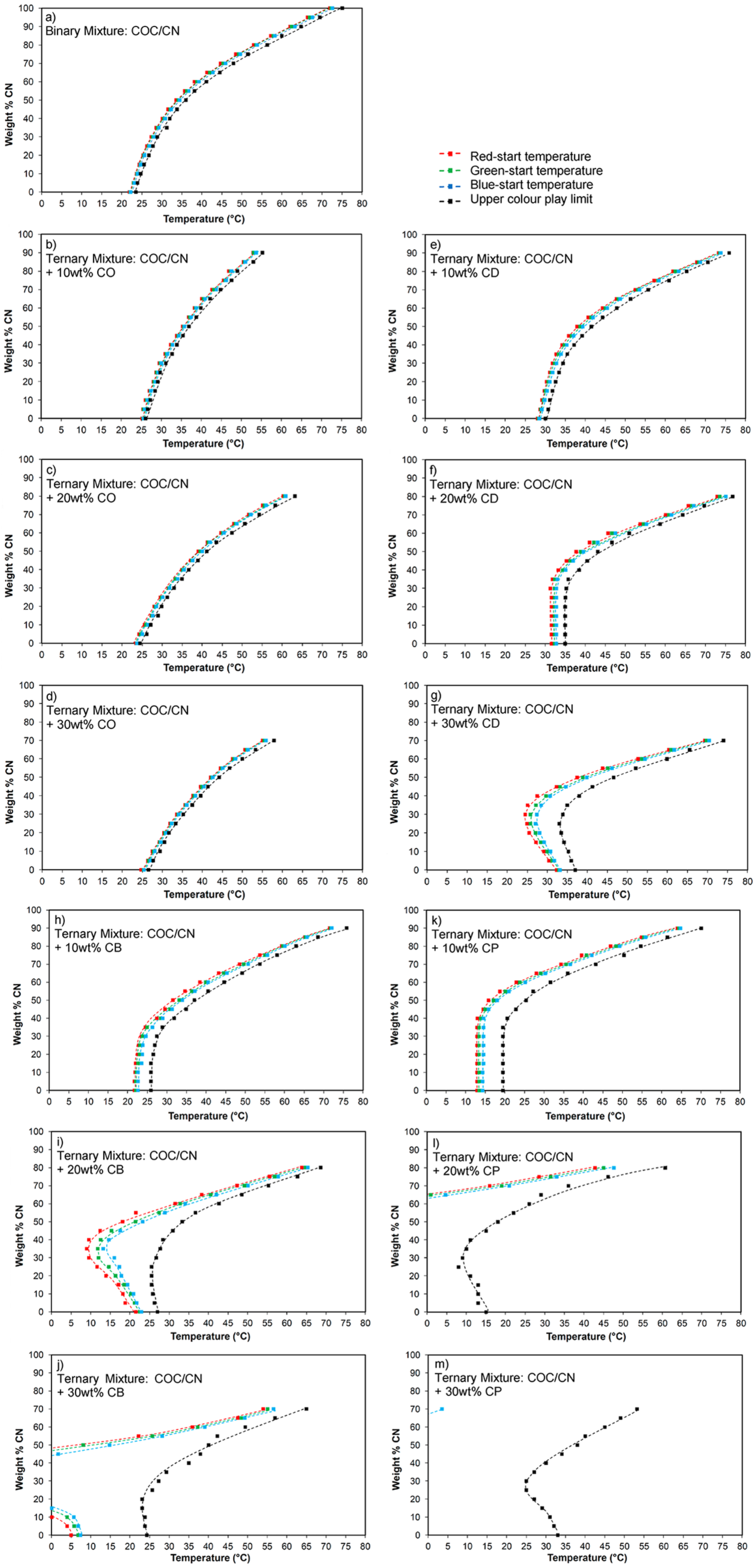


Figure 3. Relationship between composition and the red-start, green-start, and blue-start temperatures, as well as the upper color play limit for TLC mixtures as determined by the combinatorial approach.

shows the difference in color appearance of TLC mixtures with varying composition. Figure 2b shows a triplet of deposited TLC consisting of 50 wt % COC and 50 wt % CN, transitioning through its color play range, showing the points

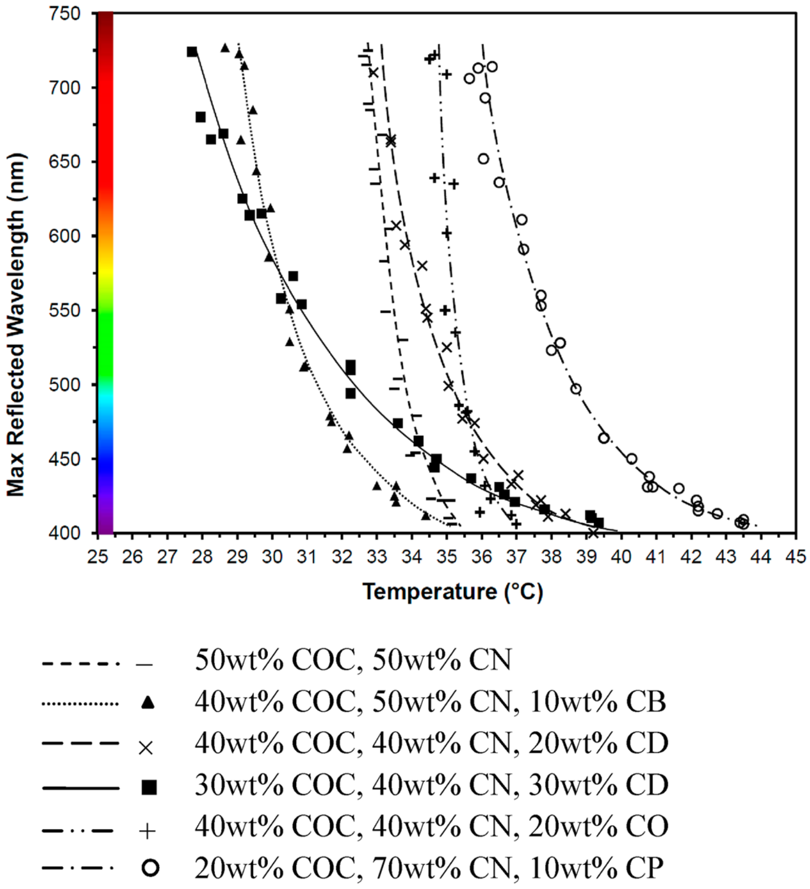


Figure 4. Maximum reflected wavelength versus temperature relationship for six selected TLC mixtures.

at which the red-start, green-start and blue-start temperatures, and the upper color play limit were visually defined.

The observed thermochromic behavior was plotted as a function of the composition of the mixture, for the binary COC/CN mixtures, and ternary mixtures containing 10 wt %, 20 wt % and 30 wt % of a third component, as displayed in Figure 3. The *y*-axis displays the weight percentage of CN in each mixture. The weight percentage of COC for each of the mixtures can easily be determined by using the formula

$$\text{wt\% COC} = 100\% - (\text{wt\% CN} + \text{wt\% C}x)$$

where Cx = CB, CD, CO, or CP.

For the binary COC/CN mixture (Figure 3a) there is a clear and predictable relationship between the wt% of CN and the temperature ranges through which the TLCs appear colored, where an increase in the CN content shifts the color play range to higher temperatures. CN has a higher melting point than COC, arising from the higher packing density between molecules. COC on the other hand, has a much lower melting temperature due to the presence of a *cis*-configured double bond in the C3-appended side chain, which disrupts high density packing.

Thermochromic behavior for the ternary mixtures seen in Figure 3b−3m show that the inclusion of a third component can significantly affect the thermochromic behavior of the resultant mixtures. As can be seen in Figure 3b−3d, the addition of CO into the binary COC/CN mixture causes little overall change in the thermochromic behavior compared to those ternary systems including the aromatic CD and CB compounds, and aliphatic short chain substituted CP (Figures 3e−3m). This is attributed to the similarities in structure between COC and CO, which both bear long unsaturated C17 side chains, such that replacement of COC with CO does little to the overall relationship between composition and thermochromic behavior. However, a small narrowing of the color play range was observed with the addition of CO. The average color play range across all of the COC/CN binary mixture compositions was found to be 2.3 ± 0.8 °C, compared to 1.6 ± 0.8, 2.0 ± 0.6, and 1.9 ± 0.5 °C for mixtures containing 10, 20 and 30 wt % CO respectively. In contrast, the addition of CD, CB and CP (Figure 3e−3m) to the binary COC/CN mixture resulted in a notable shifting of the red-start point to lower temperatures and a resultant broadening of the bandwidth for the majority of compositions. The effect became more pronounced with greater additions of the third component. In order of effect, CD had the least influence on the thermochromic behavior of the mixture; CB had a more dramatic effect, while additions of CP caused the most dramatic effect. The downward shift of the red-start temperature went beyond the limits of measurement for this technique (<0 °C) for the majority of mixtures containing 20 or 30 wt % CP. The extremity of effect appeared to increase with a decreasing bulkiness of the cholesterol derivative C3-side chains in the third component (Figure 2).

This behavior has be attributed to a depression of the smectic-A transition temperature and resultant extension of the cholesteric range to lower temperatures, with addition of these third components, including a broadening of the pretransitional effect responsible for the bulk of the thermochromic behavior. This is attributed to the introduction of cholesterol derivatives

Table 1. Comparison of Thermochromic Data Collected via the Visual Combinatorial Approach and the Graphical UV−vis Spectroscopy for Six TLC Mixtures

	red-start (°C)		green-start (°C)		blue-start (°C)		upper color play limit (°C)	
composition	combinatorial	UV−vis spectroscopy	combinatorial	UV−vis spectroscopy	combinatorial	UV−vis spectroscopy	combinatorial	UV−vis spectroscopy
50 wt % COC	33.6	32.6	34.1	33.2	34.4	33.6	36.0	35.5
50 wt % CN	Δ 1.0		Δ 0.9		Δ 0.8		Δ 0.5	
40 wt % COC	31.5	29.3	33.1	30.5	33.9	31.4	37.0	35.5
50 wt % CN								
10 wt % CB	Δ 2.2		Δ 2.9		Δ 2.5		Δ 1.5	
40 wt % COC	33.3	32.6	34.4	34	35.1	35.1	38.5	39.2
40 wt % CN								
20 wt % CD	Δ 0.7		Δ 0.4		Δ 0		Δ −0.7	
30 wt % COC	27.5	27.5	29.7	30.2	30.7	32.0	38.0	41.0
40 wt % CN								
30 wt % CD	Δ 0		Δ −0.8		Δ −0.5		Δ −3.0	
40 wt % COC	35.0	34.7	35.2	35.2	35.5	35.5	36.7	36.6
40 wt % CN								
20 wt % CO	Δ 0.3		Δ 0		Δ 0		Δ 0.1	
20 wt % COC	34.3	35.8	35.6	37.1	36.7	38.6	43.2	44.8
70 wt % CN								
10 wt % CP	Δ −1.5		Δ −2.0		Δ −1.9		Δ −1.6	

with less bulky side chains (i.e., short chain and aromatic side chains) to the binary mixture of COC and CN, which both possess long aliphatic side chain groups, thus introducing a more complex molecular packing arrangement within the system. This effect been observed under similar circumstances with CP by others.[16] It is clear that the presence of a third component, especially those cholesterol derivatives with side groups notably different in nature to those of COC and CN, can affect the thermochromic behavior of the resultant mixtures in complex ways. Important features of TLCs, including the cholesteric to smectic-A transition temperature, the size of the pretransitional effect which leads to dramatic thermochromic behavior and the helical twisting power of the mixture are all dependent on the composition and packing arrangement of the mixture, which in turn determines the overall thermochromic behavior of the system, the red-start temperature and bandwidth, and resultant sensitivity of the pitch length to changes in temperature.

Features of note for the mixtures containing either CD, CB, or CP were the regions of minimal red-start temperature and maximal bandwidths for compositions with CN between ∼30−40 wt %, with the effect becoming more pronounced with greater additions of the third component. For CN loadings both above and below this maximal point, the mixtures experienced an increase in red-start temperature and a resultant narrowing of the bandwidth. Maximal effect is seen when the three components are present in relative equal amounts by weight (i.e., at 30 wt % of the third component and 30−40 wt % of CN). The observed increase in red-start temperature with a decrease in CN content (for very low loadings of CN) within these mixtures was in direct contrast to the behavior of the binary COC/CN mixtures, where the thermochromic behavior consistently shifted to lower temperatures with a decrease in the percentage loading of CN (and an equivalent increase in the percentage loading of COC.) In these instances however, when the CN content approaches zero the mixture approaches a more ordered binary system, of COC and the third component. The interactions between these large molecules in the liquid crystalline phase is complex, and an extensive study into the effects that compositional variations have on the thermochromic behavior of TLC mixtures is beyond the scope of this paper.

Although this screening method does not provide precise transitional data, it is a valuable tool for the expedient determination of color play behavior of a variety of compositions. Limitations to this method of assessment include potential variations in temperature and heat transfer rates across the well plate, compositional variations due to the small volumes of material being deposited, and the visual and therefore somewhat subjective method for the determination of the points of color transitions. The upper color play limit was found to be especially challenging to define for mixtures with very broad blue regions. To validate the technique, the thermochromic behavior observed using the combinatorial approach was compared to data collected via a controlled approach utilizing UV−vis spectroscopy. Figure 4 displays the thermochromic behavior of six different TLC mixtures as measured via UV−vis spectroscopy, represented as the maximum reflected wavelength as a function of temperature. These six mixtures were prepared in larger quantities (1g) compared to those deposited within the well plate (20 mg) as outlined in the Experimental Procedures section. Also displayed against the *y*-axis is a representation of the color appearance of light at each wavelength. Measurements were taken in triplicate for each mixture to enable a line of best fit to be generated. Mixtures were selected such that: Each compound explored was represented; the red-start temperature occurred between 25 and 40 °C, and; a variety of color play ranges were represented.

The reflected wavelength versus temperature curves displayed here correlate well to the known behavior of TLCs.[4] The sensitivity of the mixtures (i.e., the degree of color shift with a change in temperature, or dP/dT, as represented by the gradient of the tangent to these curves) is seen to be maximal when the TLC is reflecting light at the red end of the visible spectrum, and gradually decreases as the reflected light shifts toward the blue end of the visible spectrum, that is, the sensitivity to temperature decreases as the pitch length of the helical arrangement of molecules becomes shorter, when the system is further away from the smectic-A to cholesteric transitional point.

It can be seen in Figure 4 that there are small fluctuations between repeat measurements of the same TLC composition, where the recorded temperature for any given reflected wavelength was found to vary. The width of the variation was observed to reach as high as 1 °C (for triplicate measurements of the 30 wt % COC, 40 wt % CN, and 30 wt % CD composition), however, in the majority of cases the variation was seen to be equal to or less than 0.6 °C. These variations may have been due to variations in temperature at different points on the thermoplate, minimized but not completely eliminated by the use of multiple fine wire thermocouples for temperature tracking, variations in thickness of the TLC films, or variations in the orientation of the helical structure within the cholesteric phase across the film, which in turn can affect the reflected wavelength observed. A less likely factor may be compositional variations across the film, however this was minimized by thorough mixing of the TLC mixtures at elevated temperatures upon their formation.

The wavelengths corresponding to the red-start, green-start, blue-start and upper color play points were defined at 725, 575, 500, and 400 nm respectively (see the color versus wavelength relationship in Figure 4). The average recorded temperatures at which these reflected wavelengths occurred for each TLC mixture were compared to the data recorded using the visual combinatorial approach (Table 1). It can be seen that the largest temperature discrepancy (~3 °C) between the two analytical approaches was observed with the 30 wt % COC: 40 wt % CN: 30 wt % CD mixture at the upper color play limit. This shows that the combinatorial approach for the bulk analysis of TLC mixtures is adequate for providing a reliable indication of the color play range of specific TLC mixtures, at least in the temperature ranges explored here. It must be noted that the hysteretic behavior in TLCs has not been considered in this body of work.

In addition to the thermochromic behavior of specific TLC mixtures, other factors should be taken into account when selecting TLC mixtures for use in thermal mapping applications. The data collected via the herein described combinatorial approach highlights the sensitivity of some TLC mixtures to small compositional changes. To ensure a consistent thermochromic behavior over time (or across the formulation of multiple batches of the same TLC composition), it would be ideal to select mixtures whose thermochromic behavior does not change dramatically with small compositional fluctuations. Illustrative extremes are the highly sensitive CP-containing mixtures and the less sensitive CD-containing mixtures. For example, a range of COC/CN/CD ternary mixtures (Figure 3e to g) display thermochromic behavior within the physiological temperature range (25–40 °C), and could therefore be appropriate for further study and refinement toward thermal mapping applications in the medical field. It can be seen that with 20 wt % CD content, the percentage CN can vary between 0 and 40 wt % with an almost negligible change in the thermochromic behavior of the mixture. In addition, a change in the loading of CD from 20 to 10 wt % does not cause a dramatic shift in the overall thermochromic behavior. Thus, formulations of mixtures within this particular range should provide predictable and reproducible thermochromic behavior even with slight fluctuations in their batch composition. In contrast, the COC/CN/CP ternary mixtures (Figures 3k–3m) exhibit significant changes in their thermochromic behavior with analogous variation in the composition. For example, mixtures containing 20 wt % CP exhibit a dramatic shift in color play range (by close to 15 °C) with only a 5 wt % change in the loading of CN for those compositions whose red-start temperatures lie around the physiological temperature range. Additionally, the color play range of the thermochromic behavior also changed dramatically, in both directions, as the wt% of CP was altered. Hence, formulating COC/CN/CP ternary mixtures would require tight control of composition to ensure consistent and reliable thermochromic behavior.

■ CONCLUSIONS

The above-described combinatorial technique has been used to rapidly assess the thermochromic behavior of binary and ternary TLC mixtures consisting of cholesteryl oleyl carbonate, cholesteryl nonanoate, cholesteryl oleate, cholesteryl benzoate, cholesteryl 2,4-dichlorobenzoate and cholesteryl propionate. The temperature of a custom-designed 96 well plate containing deposited TLC mixtures was easily manipulated, and the transition of each mixture through its red-start, green-start and blue-start temperature as well as its upper color play limit was visually assessed. This combinatorial technique is powerful in its simplicity and ability to facilitate the rapid assessment of thermochromic behavior for a large number of TLC mixtures. The data acquired via this simple technique possessed a strong correlation to data generated using a conventional UV–vis spectroscopic approach on bulk mixtures, at least for those mixtures whose thermochromic behavior lay between 25 and 50 °C.

The effect that incremental compositional changes has on the resultant thermochromic behavior of the TLC mixtures presented in this paper is clearly seen when the combinatorial data is displayed graphically, and highlights the complex relationship between composition of the mixtures and their resultant red start temperature, bandwidth and color play range.

While the results here have only explored a finite number of third component additions to the binary COC/CN mixture, this combinatorial technique could be readily expanded to explore more complex mixtures and encompass a wider range of compounds. With the correct experimental setup, this method could also be extended to directly ascertain raw color data from the mixtures. For example, polarizing microscopy or spectroscopy could be used in conjunction with the combinatorial technique, thus further strengthening the available data in the field.

■ EXPERIMENTAL PROCEDURE

A flat-based 8 × 12 well plate was specially fabricated from aluminum to facilitate efficient thermal conductivity. The plate measured 75 × 112 × 6 mm with wells 7 mm in diameter and 5 mm in depth with a volume capacity of 200 μL. The top of the plate and the well interiors were coated with a thin layer of black Teflon. COC, CN, CD, CB, and CP were purchased from Pressure Chemical Company, and CO from Aldrich Chemical Co., and used without further purification. Each cholesterol derivative was dissolved in GR grade Xylene from Merck at a concentration of 0.1g/mL. The appropriate amount of each component was then deposited into the allocated well using micropipet dispensers to make up a total volume of 200 μL. The xylene was then allowed to fully evaporate with warming (~70 °C), resulting in deposition of the TLC mixture (20 mg) in the bottom of each well. Further analysis was carried out immediately to avoid crystallization of deposited mixtures within the wells.

Binary mixtures of COC and CN at compositions ranging from 100 wt % COC to 100% CN were examined at 5 wt % increments. In addition to these binary mixtures, mixtures were made up containing COC and CN, and a third compound, CB, CP, CD, or CO. The third component was added at 10, 20, and 30 wt % of the total mixture. Each of the mixtures was made up in triplicate. This efficient method facilitated the rapid preparation and simultaneous screening of up to 32 separate TLC mixtures. Following evaporation of the solvent, the thermochromic behavior of each deposited mixture was determined by varying the temperature of the well plate and recording the temperatures at which each mixture visibly transitioned through its red-start, green-start and blue-start temperature, and the upper color play limit (the maximum temperature at which color is observable at the blue end of the visible spectrum). The temperature of the well plate was measured at the base of the plate and within the wells using ultrafine precision fine bare wire thermocouples and a digital thermometer. The plate temperature was cooled from 80 °C to the lower limit of 0 °C with a maximum dT/dt of −10°C/min measured. Displayed data represents the results of a single set of measurements.

A selection of compositions were also made up in bulk, by weighing the appropriate amount of each component into a glass vessel to make up a 1g mixture, and heating to 110 °C with stirring, to form a homogeneous melt. Each mixture was trapped as a thin film between two glass coverslips, and their reflectance spectrum was observed at varying temperatures. This was achieved using a Tokaihit MATS-U55S thermoplate, mounted onto the stage of an Olympus BX-61 optical microscope, which was in turn coupled via a 400 μm diameter premium grade optical fiber to an Ocean Optics QE65000 UV−vis spectrometer. The thermoplate temperature was manually variable between ambient and 50 °C, so the compositions measured using this approach were limited to those exhibiting thermochromism within this range. Spectra were recorded at increasing temperatures within the color play range of each mixture, at 0.2−0.5 °C temperature increments, allowing 30 seconds stabilization at each increment. The maximum reflected wavelength at each temperature increment was plotted against temperature.

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Author Contributions

The manuscript was written through contribution of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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ABBREVIATIONS

COC, cholesteryl oleyl carbonate; CN, cholesteryl nonanoate; CO, cholesteryl oleate; CD, cholesteryl 2,4-dichlorobenzoate; CB, cholesteryl benzoate; CP, cholesteryl propionate

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