EMISSIVE THERMOCHROMIC LIQUID CRYSTALS BY DOPING CHIRAL NEMATIC PHASE WITH LUMINESCENT PLATINUM(II) COMPLEXES

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Cholesteric liquid crystals (CLC) based on ternary mixtures of cholesteryl derivatives doped with luminescent achiral platinum(II) complex were investigated by using a combination of techniques: differential scanning calorimetry (DSC), polarizing optical microscopy (POM), variable temperature optical transmission and emission spectroscopy. The SmA-N and N*-Iso phase transitions were detected using the characterization methods mentioned. It was found that both phase transitions occur at lower temperatures when the concentration of the Pt(II) complex in the CLC mixture increases. The emission of the Pt(II) complex is blue-shifted to 532 and 575 nm in CLC matrix compared to the solid-state photoluminescence. The thermochromic response was found in the 34-37°C temperature range for CLC1+2.5% wt. Pt mixture. The same sample was selected for circularly polarized luminescence (CPL) measurements and the measured value of the dissymmetry factor g_{lum} was -2.3x10^{-2}.*

Keywords: liquid crystals, chiral nematic phase, thermochromic liquid crystals, platinum (II) complexes, circularly polarized luminescence, liquid crystal doping.

1. Introduction

Liquid crystals (LCs) are self-organized soft substances and their research is currently directed towards new composites with LCs [1-3], LC doping [4-8] and functionalized LCs [9-11].

Cholesteric liquid crystals (CLC) are an important category of liquid crystalline materials that exhibit a cholesteric phase, or actually, a chiral nematic

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phase. CLC can be generated directly from cholesterol derivatives or chiral mesogens that exhibit a nematic phase. Another method is to develop host-guest materials by mixing chiral dopants into a nematic liquid crystal (LC). The chiral nematic phase has a helicoidal arrangement that is defined by two parameters: helical pitch (p) and handedness. Left- and right-handedness refer to the molecular orientation that rotates along the helical axis. The helical pitch is the distance over which the director completes a full 360º rotation. Due to the helicoidal organization, CLC have useful optical properties such as the selective reflection of light and circularly polarized luminescence (CPL).[12] Thus, the helical pitch is related to the wavelength of the selectively reflected light (λ) and the average refractive index of the material (n), using the following relationship:

$$\lambda = np$$

The capacity of CLC to selectively reflect light, along with their responsiveness to temperature and other external influences (pressure, light, etc.), renders them highly valuable in a diverse array of applications, spanning from display technology to sensors and smart windows. CLC based on mixtures of cholesteryl derivatives are well known for their ability to display thermochromic behavior depending on the composition of the individual components. The decrease in temperature produces the unwinding of the helical structure, which leads to an elongation of the pitch length. When the temperature is lowered, the liquid crystal first exhibits a reflection of blue light, with pitch lengths that are relatively short. As the temperature falls even further, the reflected wavelength changes towards the red domain of the spectrum because the pitch length increases. This change of color happens above the observed transition temperature from Smectic A (SmA) to chiral nematic (SmA*–N*).[13]

Doping CLC with non-mesogenic metal complexes provides a versatile approach to improving their characteristics and broadening their potential uses [14, 15]. Metal complexes offer enhanced luminescence, greater stability, tunable optical characteristics, and increased functional diversity, making doped CLCs particularly appealing for various applications. For example, non-mesogenic Eu(III) complexes have been used as dopants in CLC to produce strong circularly polarized emission.[16] Non-mesogenic dopants in liquid crystals (LCs) typically decrease the temperature range at which the mesophase occurs by interfering with the molecular arrangement.[17] However, when present in small concentrations, certain highly anisotropic dopants, such as specific ferromagnetic nanoparticles (NP) and multiwall carbon nanotubes (MWCNT), [18, 19] can increase the temperature at which the nematic-isotropic transition ($T_{N\text{-}Iso}$) occurs.

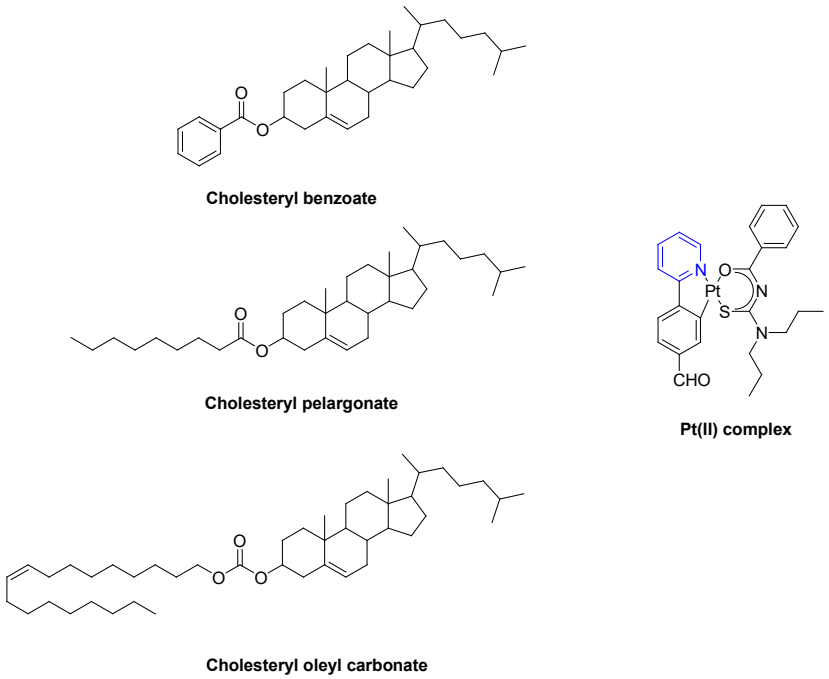


Fig. 1. The structure of the compounds employed in this study.

This paper presents the study of the emission properties of a luminescent organometallic Pt(II) complex doped in ternary CLC mixtures consisting of the following cholesterol derivatives: cholesteryl oleyl carbonate, cholesteryl pelargonate, and cholesteryl benzoate (Figure 1). The selection of these compounds was based on their broad usage in producing cholesterol-based thermochromic CLC mixtures. Additionally, they exhibit a transition into the cholesteric phase at varying temperatures, and are more cost-effective compared to other commercially available chiral LC or dopants.[20]

2. Experimental part

2.1. Preparation of CLC mixture

The CLC mixture with thermochromic behaviour in the 37-40 ºC temperature range was prepared by mixing 0.3 g of cholesteryl oleyl carbonate, 0.6 g of cholesteryl pelargonate, and 0.1 g of cholesteryl benzoate in a vial (sample code CLC1). To this mixture, a volume of 3 mL of dichloromethane was added, in order to dissolve all three organic compounds, ensuring their homogeneous mixing. The resulting mixture was heated on a hotplate with continuous stirring, at 70 ºC, until, after successive weighing, the sample weight was found to be constant, indicating the evaporation of solvent used. The preparation process is schematically represented in Figure 1. Separately, for

polarized emission measurements, a CLC mixture with thermochromic behavior in the 29-32 ºC temperature range was prepared by using 0.7 g of cholesteryl oleyl carbonate, 0.1 g cholesteryl pelargonate, and 0.2 g of cholesteryl benzoate by following the same procedure (sample code CLC2).

2.2. Preparation of CLC mixture doped with Pt (II) complex

Two different mixtures of the CLC1 doped with a luminescent platinum complex were prepared (Figure 1), first mixture having a concentration of 5% of Pt complex and the second mixture having a concentration of 2.5% of Pt complex. For both mixtures, the required amounts of CLC1 and Pt complex were taken in a vial and dissolved in 0.5 ml of dichloromethane. The solvent was removed by heating at 70 ºC until the weight remained constant. A total amount of 100 mg was prepared for each mixture. The Pt(II) complex was prepared as reported elsewhere.[21]

2.3. Physical measurements

The temperature dependency of the selective reflection band was investigated by measuring reflectance spectra with a fiber optic spectrometer. The samples were spread onto glass slides and then covered with a second glass slide. The cell was placed against a black background for emission and reflection measurements. The cells thickness was measured with the interferences obtained when recording the reflection spectra. The equipment used for the measurement of spectra is described as follows: the signal is taken by using an optical microscope Nikon 50iPol through an optic fiber connected to QE65000 Pro OceanOptics detector. For the optical transmission and selective reflection spectra, the sample was irradiated with the light coming from a Nikon Halogen D-LH lamp attached to a Nikon 50iPol microscope, while for the emission spectra, the sample was irradiated with UV light from the LED source LLS 365 nm Ocean Optics.[22, 23]

The temperature at which the sample was studied was controlled with the help of a Linkam THMS600 heating plate connected to a TMS94 temperature control device, and the heat rate (respectively, the cooling rate used) was 2 ºC/minute. For the optical transmission and emission spectra, the measurements were taken a minute after the desired temperature was reached by the heating plate, to be sure that the temperature of the sample was the same as the one displayed, while for the selective reflection spectra, the measurements were performed 5 minutes after the desired temperature was reached by the heating plate, to ensure the uniform heating of the sample in all its mass.

The program used for the data collection was SpectraSuite. The emission and selective reflection spectra are a type of spectra in which intensity (expressed in arbitrary units/ by normalized values) is represented as a function of wavelength (expressed in nanometers). The intensity of the transmitted light at

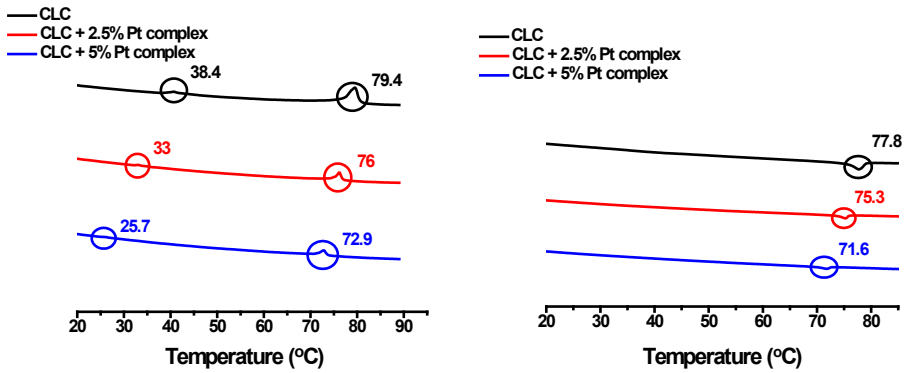
λ=650 nm was taken for the optical transmission measurements. The final result is a plot of the intensity of the transmitted light as a function of temperature (in ºC).

The influence of Pt(II) complex on the phase transition temperature was investigated with differential scanning calorimetry (Diamond, Perkin Elmer) equipped with Intracooler 1P (Perkin Elmer). Two mixtures of CLC+Pt(II) complex, one filled with 2.5% wt. Pt and one with 5% wt. Pt, were investigated, respectively. CLC was used as reference. Samples of a mass between 15.5 and 21.5 mg were filled into aluminum crucibles without lids and heated with a heating rate of 10 °C min^{-1} from 20 to 90 °C. The final temperature was held for 5 min and subsequently, the samples were cooled to 20 °C again with a cooling rate of 10 °C min^{-1} and heated up again to 90 °C with 10 °C min^{-1}. The measurement was performed in a nitrogen atmosphere (flow rate of 20 mL min^{-1}) to avoid any oxidative degradation. For polarized emission measurements the CLC+5%Pt sample was filled into a planar cell (Instec, 15 µm thickness). For circularly polarized emission measurements, a quarter-wave plate was used and the polarizer was set at 0º. The intensity of the signal at 530 nm was measured by rotating the plate at -45º and +45º.

3. Results and Discussion

3.1. Thermal behavior

The thermal behavior of the samples was investigated by DSC and polarized optical microscopy (POM) observations and correlated with optical transmission measurements.



(a) (b)

Fig. 2. Comparative DSC curves of all the three CLC mixtures on heating (a) and cooling (b).

When examining the DSC curves obtained during heating, it is possible to observe two peaks for all three mixtures. The first peak, occurring at lower

temperatures, corresponds to the SmA-N* transition (Figure 2). The second peak, occurring at higher temperatures, corresponds to the N*-Iso transition. Observing the CLC mixture doped with 5% Pt complex, one can notice a rather feeble peak at approximately 25 ºC, on cooling run, indicating the SmA-N* transition. This behavior was confirmed by visual observations on the color change of samples near the SmA-N* phase transition (Figure 3). The DSC curves obtained during cooling clearly show the N*-Iso transition for all three samples. During both heating and cooling, it is evident that the transitions occur at lower temperatures when the concentration of the Pt (II) complex in the CLC mixture increases. This shift to a lower temperature indicates a decrease in the temperature range where the thermochromic effect, specifically the SmA-N* transition, can be observed.

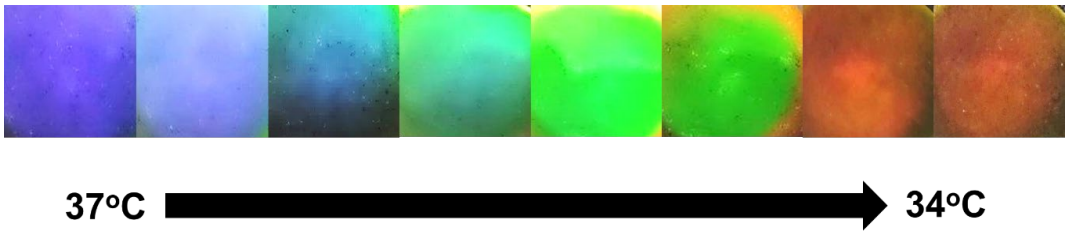


Fig. 3. Thermochromic effect for the CLC+2.5%Pt mixture.

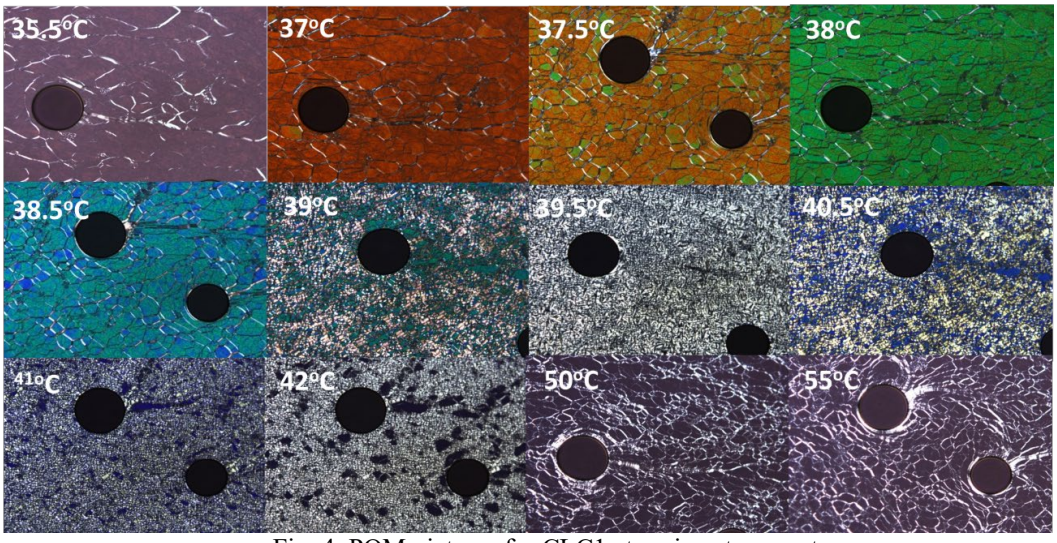
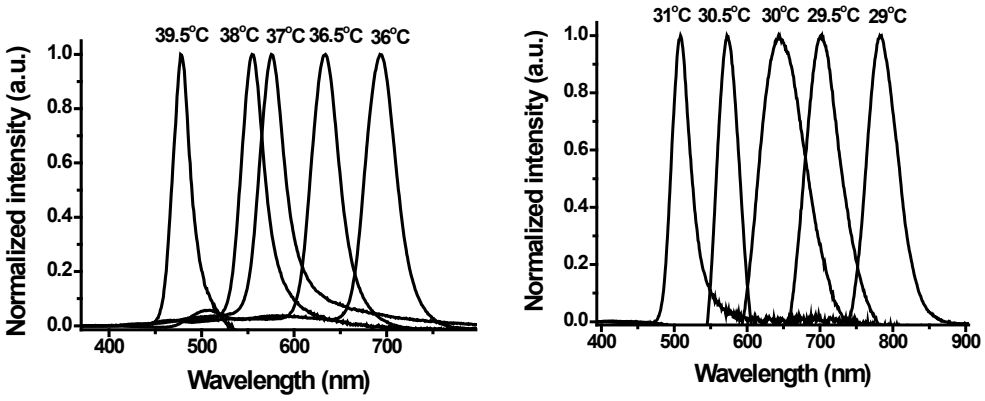


Fig. 4. POM pictures for CLC1 at various temperatures.

Additionally, it is worth noting that the peaks decrease in size in the following order: simple CLC mixture, CLC mixture doped with 2.5% Pt complex, and CLC mixture doped with 5% Pt complex. However, a more significant change

in the SmA-N* transition temperature was observed when compared to the change in the N*-Iso transition temperature values.

The selective reflection spectra of the simple CLC1 and CLC2 mixtures were measured, and the obtained data was compared to the initial expectations (Figure 5).



(a) (b)

Fig. 5. Reflection spectra of the CLC1 (a) and CLC2 (b) mixtures recorded upon heating. The rate of the temperature change is 2 °C/min.

The CLC exhibited the desired thermochromic effect within the specified temperature range, with the peak wavelength decreasing as the temperature increased. This resulted in a color change from red at lower temperatures to blue at higher temperatures. (Figure 5) The POM pictures taken under UV irradiation for both doped samples demonstrate the good miscibility of the Pt complex in CLC mixtures. However, it is worth noting that some separations of crystallites of Pt complex have been observed in the 5% doped sample (Figure 6).

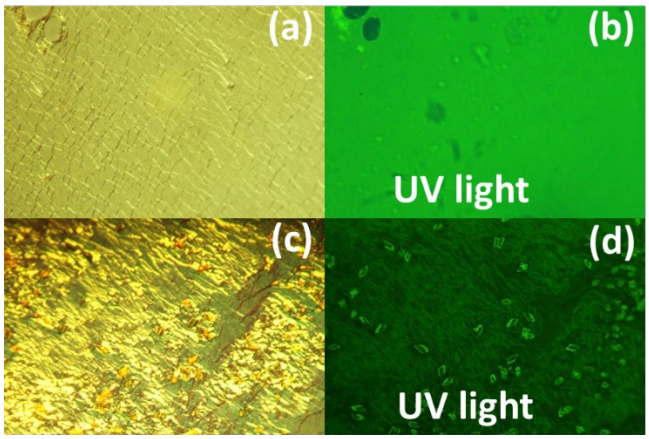
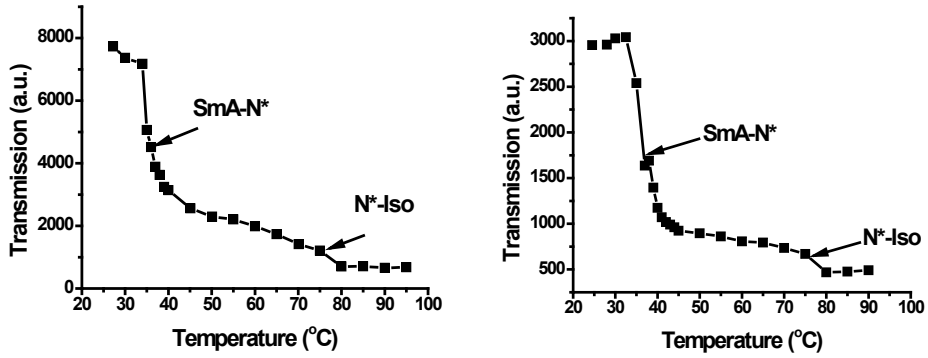


Fig. 6. POM textures of CLC1+2.5%Pt at 41°C (a, b) and CLC1+5%Pt at 37°C (c, d).

By measuring the instensity of the transmitted light (λ = 650 nm) through the cells containing the two CLC mixtures doped with Pt(II) complex, two phase transitions were clearly observed (Figure 7). For CLC1+2.5%Pt mixture, the transition temperatures are 74.9°C and 36.1°C corresponding to N*-Iso and SmA-N* phase transitions, respectively.



(a) (b)

Fig. 7. The optical transmission spectra for the CLC mixtures doped with Pt (II) complex: CLC1+2.5%Pt (a) and CLC1+5%Pt (b).

For the mixture with higher content of Pt(II) complex, the two transition were found around 72.4°C and 35.1°C. The $T_{N^*\text{-Iso}}$ and $T_{SmA\text{-}N^*}$values taken at the inflection point of the curve are slightly lower than the values detected by DSC for the CLC1+5%Pt mixture and could be attributed to the different heating rates used for the two experiments, 2°Cmin^{-1} for optical transmission and 10°Cmin^{-1} for DSC as well as the partial crystallization of the Pt(II) complex during the experiment. On the other hand, the corresponding values of the transition temperatures observed for CLC1+2.5%Pt agree well with those obtained by DSC measurement.

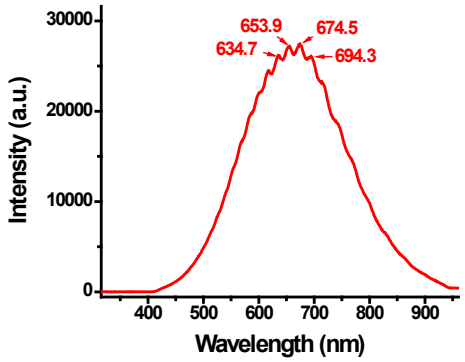
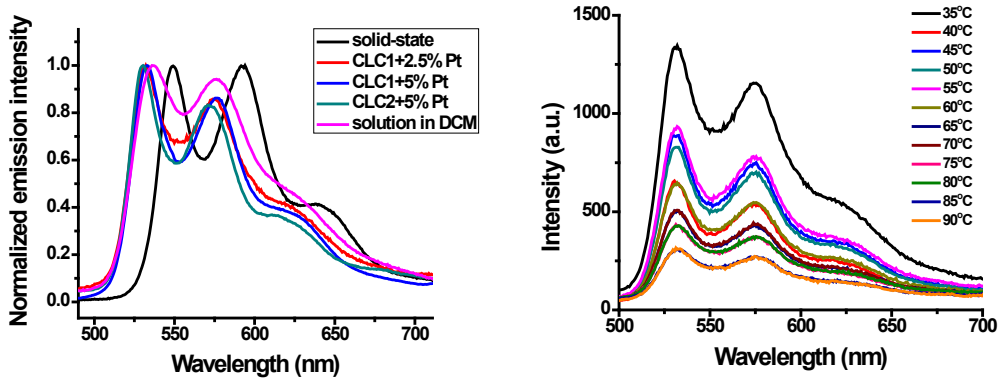


Fig. 8. Interferences used for the determination of the CLC1+2.5%Pt layer thickness.

The CLC layer thickness of the cells used for selective reflection spectra and optical transmission measurements was measured by using the interference spectra (Figure 8) and calculated by using the following relationship: $m_n\lambda_n=2d_n\sin\theta n$, where m_n is the diffraction order at interference maximum λ_n and n the mean value of the refractive index. If $2d_n\sin\theta n$=const. and $m_1\lambda_1 = (m_1+1)\lambda_2$, then $m_1= \lambda_2/(\lambda_1-\lambda_2)$.[24] The mean refractive index was measured by using an Abbe refractometer at room temperature giving n=1.5062. A layer thickness of around 4 μm was obtained in each case.

3.2. Characterization of the emission properties

The emission spectra of the Pt(II) complex were recorded in various media: solid-state, solution in dichloromethane (DCM) and doped in CLC mixtures. A blueshift of the emission maxima was observed in solution (537 and 536 nm) compared to their position in solid-state (550 and 591 nm), which could be due to the existence of non-covalent interactions (Pt···Pt, π-π and C-H···π) in solid-state.[25] By analyzing the spectra of Pt(II) complex in solid-state and solution, it becomes evident that the emission spectrum of the Pt complex doped in both CLC mixtures closely resembles the one recorded in DCM solution: 532 and 575 nm for CLC1+2.5%, 532 and 572 nm for CLC1+5%Pt,. The slight change of the position of emission maxima in CLC mixtures when compared to DCM solution could be assigned to different polarities between the DCM solvent and CLC matrix. This observation confirms the good miscibility of the Pt(II) complex in the CLC mixture. It is worth noting that the emission maxima are located around 530 nm, which corresponds to the green color in the visible spectrum. For comparison purposes, a CLC2+5%Pt mixture was prepared, and its emission was recorded (Figure 9).



(a) (b)

Fig. 9. The emission spectra of Pt(II) complex in different states (a) and of CLC1+2.5% Pt mixture at different temperatures, recorded on heating (b).

The emission maxima are located at 530 and 572 nm for CLC2+5%Pt, the slight difference compare to the related sample CLC1+5%Pt is attributed to the difference in the chemical composition of the three cholesteryl derivatives.

Upon analyzing the emission spectra for CLC mixture doped with 2.5%Pt complex on heating from 35ºC up to 90ºC, it becomes evident that the position of the emission maxima remains constant regardless of any temperature variations. Furthermore, there is a general trend of decreasing emission intensity as the temperature rises. This correlates well with the displayed POM images below (Figure 10).

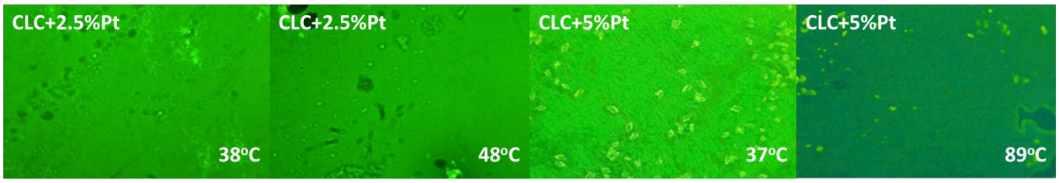


Fig. 10. POM images of the two mixtures CLC+2.5%Pt and CLC+5%Pt at two different temperatures recorded under irradiation with UV light (365 nm).

CLC1+2.5%Pt mixture was selected for CPL investigation. The CPL spectra were measured using a detector and a combination of an achromatic quarter wave-plate and polarizer. In order to measure left- or right-handed components of CPL, the quarter wave-plate was rotated by ±45° with respect to the polarizer axis. The strategy used in this work to achieve CPL is to get CPL-active CLC by doping CLC with an achiral emitter, which is the platinum(II) complex. The CLC1+2.5%Pt mixture was heated up to 35ºC in the thermochromic range and excited using 365 nm LED source. The chiral materials emit different intensities in the excited state of left- and right-handed circularly light. The CPL is characterized by the luminescence dissymmetry factor (g_{lum}) which is defined with the following relationship:

$$g_{lum} = 2(I_L - I_R)/(I_L + I_R)$$

where I_L is the intensity of left-handed CPL and I_R is the intensity of right-handed CPL. A zero value for g_{lum} denotes that the light has no circular polarization and a +2 or -2 values denotes that the light has a complete left- or right-handed circular polarization.[26] Whereas the CPL with the opposite handedness is totally transmitted, the CPL with the same direction as the helical twist of CLCs is totally reflected when the emission peak overlaps with the reflection band of CLCs. Therefore, placing the emitter's luminescence at the center of the photonic bandgap of CLCs is likely to result in a significantly higher g_{lum} value.[27] The emission band of the Pt(II) complex used in this study is located in the 530 – 650 nm wavelength range, which fits well with the position of the bandgap of the

CLC1+2.5%Pt mixture at 35ºC (Figure 11). The measured value of g_{lum} is -2.3x10^{-2}, which is comparable with the values found in general for chiral metal complexes (10^{-2} – 10^{-4}) [28] or for chiral metallomesogens based on platinum(II) complexes.[29-31].

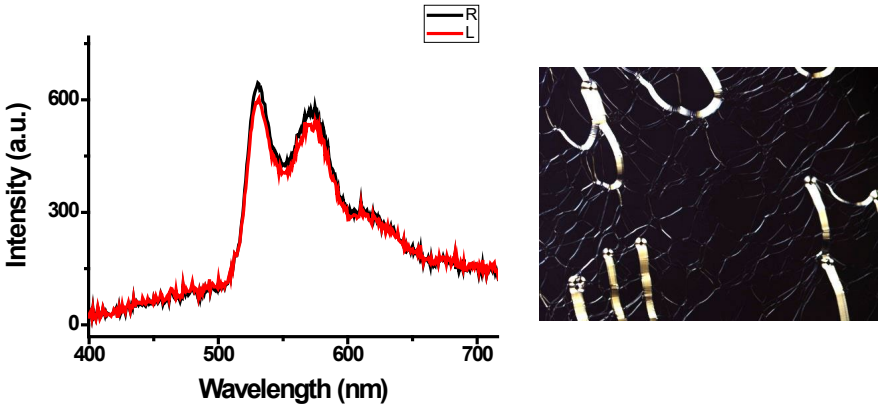


Fig. 11. Spectra of left- and right-handed circularly polarized luminescence recorded at 35 °C for CLC1+2.5%Pt mixture (inset: POM picture of the planar cell used for the CPL measurement).

4. Conclusions

In this work, we prepared two cholesteric mixtures CLC1 and CLC2 with thermochromic responses on different thermal ranges (37-40ºC and 29-32ºC). CLC1 mixture was doped with an achiral emissive platinum(II) complex in two concentrations: 2.5 and wt. 5%. The effect of doping concentration on the SmA-N* and N*-Iso transition temperatures and thermochromic behavior were investigated by using a combination of DSC, POM and optical transmission measurements. Based on the POM observations and emission measurements, CLC1+2.5%Pt sample was observed to have the Pt(II) complex homogeneously dispersed in the LC matrix while CLC1+5%Pt showed partial crystallization of the dopant. The SmA-N* and N*-Iso phase transitions occur at lower temperatures when the concentration of the Pt(II) complex in the CLC mixture increases. Therefore, the thermochromic response was found in the 34-37ºC temperature range for CLC1+2.5%Pt mixture. The same sample was selected for CPL measurements and the measured value of the dissymmetry factor g_{lum} was -2.3x10^{-2}, which is comparable with the values found in general for chiral metal complexes (10^{-2} – 10^{-4}) or for chiral metallomesogens based on Pt(II) complexes.

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