EFFECT OF MWCNT DOPING ON THE T_{NI} TRANSITION TEMPERATURES AND EMISSION BEHAVIOR OF A NON-MESOGENIC LUMINESCENT PLATINUM(II) COMPLEX IN NEMATIC LIQUID CRYSTAL 5CB

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5CB liquid crystal and multiwalled carbon nanotubes (5CB-MWCNTs) composites doped with luminescent platinum(II) complex were investigated by means of differential scanning calorimetry (DSC), polarizing optical microscopy (POM), emission spectroscopy and optical transmission. MWCNTs have no effect on the photoluminescence spectra of the platinum(II) complex. The nematic to isotropic phase transition was detected for all composites using the techniques mentioned. It was found that the values of T_{NI} obtained for the doped samples with platinum(II) complex by emission and optical transmission measurements in planar orientation agree well with those obtained by DSC. The low value of the order parameter for the platinum(II) complex in 5CB (S=0.08) is most likely the result of an alignment mismatch between the molecules of the complex and 5CB.

Keywords: liquid crystal, multiwall carbon nanotubes, luminescence, phase transitions, polarized optical microscopy, platinum complex.

1. Introduction

Liquid crystals (LCs) are a highly adaptable category of smart materials that possess remarkable optical, electrical, mechanical, and biological characteristics. They also exhibit responsiveness to multiple stimuli, making them well-suited for

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a wide variety of applications. [1] The distinct characteristics are directly associated with the specific arrangement in various liquid crystalline phases (mesophases). The properties of LCs can be significantly enhanced through their incorporation with other materials. [2-4]

Novel electro-optical and physico-chemical properties for systems based on LCs can be obtained by doping various nanoparticles, polymers, quantum dots, dyes, as well as organic or inorganic compounds mostly into the nematic liquid crystals. The resulting composite materials may exhibit distinct properties compared to pure LCs. Among the different nanoparticles used for doping LCs, carbon nanotubes (CNTs) dispersed in LCs are the most studied class of composite materials. [5, 6] Both single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) have been widely used to prepare composite materials taking advantage of their interesting properties such as high electrical and thermal conductivities or high tensile strength. In this way, LCs doped with small amounts of CNTs can substantially modify their electrical and optical properties. The integration of SWCNTs and MWCNTs in nematic and other types of liquid crystals as well as the effects of alignment and supramolecular organization resulting from orientational coupling between CNTs and the LC matrix were recently reviewed.[7-9]

Moreover, various host-guest systems can be obtained by dispersing organic or metal complexes [10, 11] as dopants in liquid crystalline matrix with a significant impact on their phase transition temperatures, dielectric behavior, order parameter and photophysical properties.[12, 13] Non-mesogenic metal complexes have been utilized as dopants in LCs with the aim to transfer chirality to the nematic phase [14-17] or to investigate the resulting linearly [18] or circularly polarized emission [19] as well as the changes in the electrical or dielectric properties of the composite materials.

4’-pentyl-4-biphenylcarbonitrile (5CB) is a nematic liquid crystal at ambient temperature and largely explored as a liquid crystalline host to study the effect of intermolecular interactions, ranging from dipole-dipole interactions, π-π stacking, hydrogen-bonding or aggregation with different doping materials. For example, Mashke et al. studied the effect of doping 5CB with n-dodecyl-2-hydroxy-1-naphthaldimine and other salen Schiff base derivatives and their nickel(II) and iron(III) complexes on the nematic to isotropic transition temperature by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and UV-visible spectroscopy, evidencing significant changes in the thermal behavior and orientational order parameters.[20, 21]

By doping derivatives of benzoic acids into 5CB liquid crystals, the temperature range at which the liquid crystals exhibit nematic behavior is expanded. This indicates that adding a dopant can result in a more stable liquid crystalline material with an enhanced range of temperatures in which it can operate effectively [22]. The nature and concentration of organic or CNTs dopants can also impact the dielectric parameters of 5CB.[23, 24] The interaction of MWCNTs with 5CB was examined by Peterson et al. [25] using dielectric relaxation spectroscopy. At lower frequencies, the MWCNTs undergo reorientation in conjunction with the 5CB molecules, whereas higher frequencies restrict the reorientation of MWCNTs.

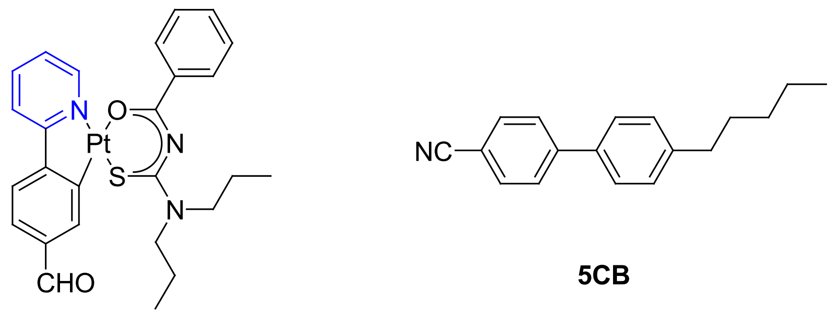
Luminescent materials that exhibit linearly polarized emission can be also prepared by doping metal complexes into liquid crystals [26] as an alternative to luminescent metallomesogens (liquid crystals based on metal complexes). [27-31] In this study, we took advantage of the excellent emission properties of the platinum(II) complex (Scheme1) as well as its good miscibility with the 5CB host. The nematic to isotropic phase transition in 5CB-MWCNTs-Pt complex composites was investigated by DSC, POM, emission spectroscopy and optical transmission measurements.

2. Experimental

The samples were prepared by mixing 5CB nematic LC with MWCNTs with the average length of 10 μm inner diameter of 2b = 4.5 nm and the outer diameter 2a = 10 nm. The nanotubes were dispersed in toluene and sonicated for several hours until a good dispersion was obtained. The solution was mixed with 5CB and placed in a laboratory clean room to evaporate the toluene. The mixture was weighed daily until the weight was constant and the evaporation process was finished. The resulted nanotubes concentrations were 0.07 wt%, 0.16%, 0.26% and 0.61 wt%. The 5CB-MWCNT mixtures with various concentrations were doped with 2 wt% Pt complex by mixing the appropriate amounts in dichloromethane (DCM) and ultrasonicated for 30 min. The Pt complex was prepared according to the procedure reported elsewhere and is easily soluble in DCM (Scheme 1).[32] The remaining solvent was removed by heating the samples at 50oC until constant weight.

For the measurement of the emission and optical transmission in planar orientation, the prepared mixtures were used to fill 15 μm thick planar aligned cells (Instec).

Differential scanning calorimetry (DSC) experiments were undertaken using a Diamond DSC calorimeter (Perkin Elmer) equipped with Intracooler 1P (Perkin Elmer), and dry nitrogen gas was used for purging the sample ($20 ml min^{-1}$). The heating and cooling rates were $5^{o}C min^{-1}$ unless indicated otherwise. Samples in the range of 5–10 mg were sealed in aluminium pans. DSC experiments were performed in the temperature range 20–45°C to determine the nematic to isotropic transitions of neat 5CB and of its blends with MWCNTs as well as with the platinum(II) complex.



Scheme 1. Chemical structure of platinum(II) complex and 5CB used in the present study.

For the optical microscopy experiment (POM), a Nikon 50 iPOL microscope with polarized light was utilized. 100X or 200X magnifications were employed and digital pictures were acquired using a digital camera (DS-Fi1, Nikon) and NIS Elements software. A sample hot stage (Linkam Scientific Instruments, Model THMS600) connected to a programmable temperature controller (Linkam, Model TMS94) was employed for temperature variable measurements. Untreated glass slides were used for POM observations. POM textures were captured when cooling the isotropic liquid samples (~40°C) down to room temperature at a ramp rate of 2°Cmin^{-1}. The photoluminescence spectra were recorded for the samples sandwiched between two glass slides, with the OceanOptics QE65PRO spectrometer attached to the polarizing optical microscope and using a Nikon Intensilight excitation source and UV-2A filter (excitation range 330-380 nm). The same setup was utilized to capture POM picture with UV light irradiation. [33]

3. Results and Discussion

3.1. Investigation of the nematic to isotropic phase transition of 5CB and 5CB-MWCNTs composites doped with platinum(II) complex by POM and DSC

The textures of 5CB using a polarising optical microscope were seen and found to be consistent with previous findings. The platinum(II) complex was mixed with 5CB at 2 wt% concentration to achieve highly emissive dye-doped LCs. Higher concentration of platinum(II) complex above 2% in 5CB resulted in the formation of aggregates visualized by POM and upon irradiation with UV light. The POM images of 5CB-MWCNTs composites doped with 2 wt% Pt all displayed typical nematic optical textures (Figure 1). Moreover, the irradiation with UV light confirmed the good miscibility of platinum(II) complex in 5CB without forming any aggregates of carbon nanotubes.

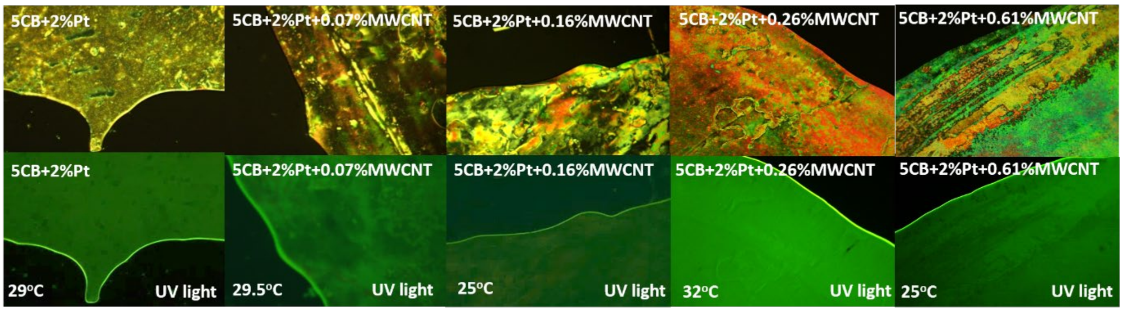


Fig. 1. POM pictures in normal light and with UV irradiation (365 nm) of composite materials.

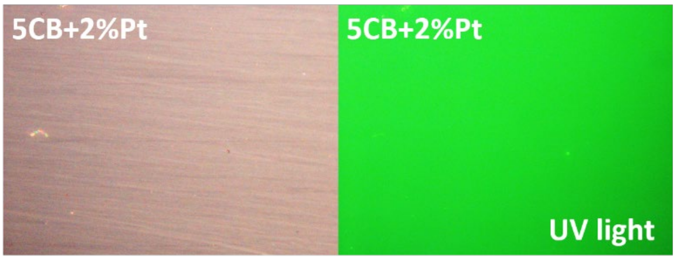


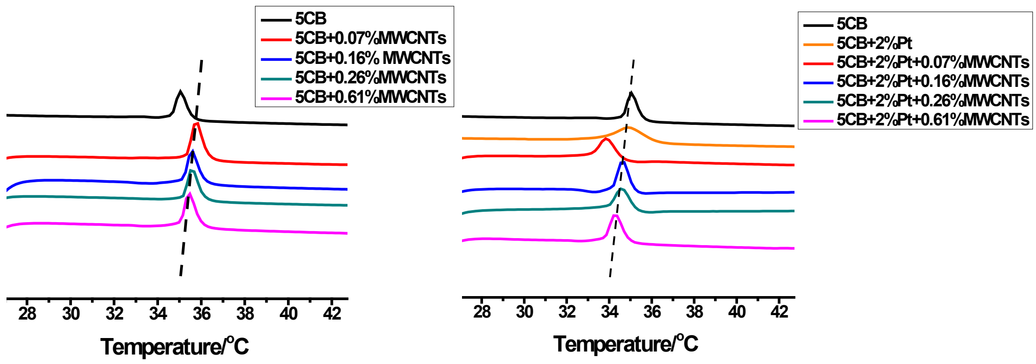
Fig. 2. POM picture of planar cell filled with 5CB+2%Pt composite material in normal light and under UV irradiation (365 nm).

The temperature range at which the 5CB liquid crystal exhibits nematic phase is from 24 °C to 35 °C. The phase transition temperatures of pure 5CB were analyzed by DSC and POM and compared to the existing literature. The transition temperatures of the nematic liquid crystal 5CB and the effect of the concentration of CNTs in dispersions of 5CB have been extensively investigated by DSC and several other techniques, including dielectric spectroscopy, UV-visible spectroscopy, etc. For example, Verma et al.[34, 35] found that the isotropic to nematic transition temperature of 5CB (35.1ºC) decreases with the increase of the concentration of SWCNTs for 0.02 wt% (33.4ºC) and 0.05wt% (32ºC) SWCNTs when measured by dielectric spectroscopy. The same blends when measured by DSC gave the following transition temperature for nematic to isotropic: 34.5ºC (5CB), 33.6ºC (5CB+SWCNTs 0.02 wt%) and 33.4ºC (5CB+SWCNTs 0.05 wt%), evidencing the decrease of the clearing temperatures as a result of doping with SWCNTs.

Ibramigov et al. [36] reported that at higher concentration of SWCNTs (0.5 wt%), the clearing temperature of composite material has increased to 37.1ºC from 35.2ºC for pure 5CB when measured by POM and dielectric spectroscopy, due to an increase in the order parameter of 5CB as a result of parallel orientation of SWCNTs to the LC director.

Lebovka et al. [37] investigated the impact of MWCNTs on low-temperature phase transformations in 5CB by DSC with no particular focus on the isotropization temperature. The nematic to isotropic transitions were observed at temperatures around 35.4ºC. While the DSC peaks were found to be narrow in the absence and low concentration of MWCNTs (0.1%), at higher concentration (1%) these were broader, with no discussion related to changes of T_{NI}.

Figure 3a shows the DSC themograms obtained for the second heating cycle for 5CB and 5CB-MWCNTs samples with the scanning rate of 5ºCmin^{-1}. DSC traces of these samples exhibited a single peak, attributed to the nematic to isotropic transition, in the temperature range from 25 to 45 °C. In these experimental conditions, the nematic to isotropic transition for pure 5CB was found at 35.05 ºC (Table 1). The samples with 0.07, 0.16, 0.26 and 0.61 wt% MWCNTs show T_{NI} at 35.75, 35.58, 35.55 and 35.48 ºC, respectively (Table 1). The T_{NI} was enhanced by incorporation of MWCNTs in 5CB for all samples and the largest shift of 0.70 ºC was observed at lowest concentration (0.07 wt%). However, increasing the concentration of CNTs in 5CB leads to a slight reduction of the difference between the T_{NI} recorded for 5CB and 5CB-MWCNTs samples. The observed enhancement of T_{NI} appears to be influenced by the anisotropic alignment of liquid crystal molecules on MWCNTs, as it has been established in literature.[38]



(a) (b)

Fig. 3. Effect of MWCNTs concentration on the nematic to isotropic transition temperature of 5CB (a) and its composites with platinum(II) complex (b).

The parallel orientation of MWCNTs to the nematic director leads to higher order parameter and, consequently, to increased clearing points. Similar results were found for dispersions of MWCNTs in nematic E7, a commercial mixture of 5CB, 7CB, 8OCB and 5CT.

The phase diagram of E7-MWCNTs dispersion based on POM observations and DSC measurements, revealed a significant enhancement of T_{NI} in a very narrow range of concentrations of MWCNTs (0.1-0.2 wt%) and a rapid decline of T_{NI} at higher values (0.3-~1 wt%).[39]

Table 1

Transition temperatures for 5CB and its composites with MWCNTs and platinum(II) complexes, obtained by DSC (second heating run, T_{peak})

Sample	T_{N-I}(°C)	ΔT(°C)
5CB	35.05	0
5CB+0.07%MWCNT	35.75	0.70
5CB+0.16%MWCNT	35.58	0.53
5CB+0.26%MWCNT	35.55	0.50
5CB+0.61%MWCNT	35.48	0.43
5CB+2%Pt	34.87	-0.18
5CB+2%Pt+0.07%MWCNT	33.89	-1.16
5CB+2%Pt+0.16%MWCNT	34.63	-0.42
5CB+2%Pt+0.26%MWCNT	34.59	-0.46
5CB+2%Pt+0.61%MWCNT	34.29	-.076

When 5CB was doped with 2 wt% Pt complex, a slight decrease of T_{NI} was observed by DSC, from 35.05 °C for pure 5CB to 34.87 °C, respectively. The size and the molecular geometry of the platinum(II) complex as well as the possible interactions of 5CB molecules via the cyano groups with the metal center in axial positions rendered the order degree to decline compared to pure 5CB. Interestingly, the incorporation of MWCNTs lead to further decrease of T_{NI} with the highest difference observed for the sample doped with the lowest amount of carbon nanotubes (5CB+2%Pt+0.07%MWCNTs). The values of T_{NI} recorded for the other samples doped with the platinum(II) complex followed the same trend as observed for the 5CB-MWCNTs composites.

3.2. Investigation of the nematic to isotropic phase transition of doped 5CB by using emission spectroscopy and optical transmission measurements

Additionally, the investigation of the phase transition in 5CB doped with 2 wt% platinum complex sample (5CB+2%Pt) was undertaken by measuring the emission intensity and optical transmission in a planar cell. The emission spectra were measured in the 25-50 ºC temperature range with steps of 0.5ºC. In 5CB, the platinum(II) complex display significant emission that is red-shifted in solid-state due to the polarity of the 5CB solute. The emission band of platinum(II) complex dissolved in 5CB has characteristic vibronic structure with maxima around 535 and 575 nm and a shoulder at about 630 nm. The same features were preserved in the 5CB doped with MWCNTs composites (Figure 4), suggesting the absence of any interactions of platinum(II) complex with the carbon nanotubes. Figure 5a presents the variation of emission intensity measured at 535 nm as a function of temperature while figure 5b shows the emission spectra of 5CB+2%Pt sample recorded in the 25-50 ºC temperature range when measured in the planar cell. No shift of the emission was detected on heating the sample. However, the emission intensity values decrease with increasing the temperature since the emission of platinum(II) complex is quenched at higher temperature due to a non-radiative deactivation process. An abrupt change in intensity was seen near the transition from the nematic phase to the isotropic phase. The T_{NI} measured at the inflexion point is about 34.6 ºC that is close to 34.87 ºC value recorded by DSC technique.

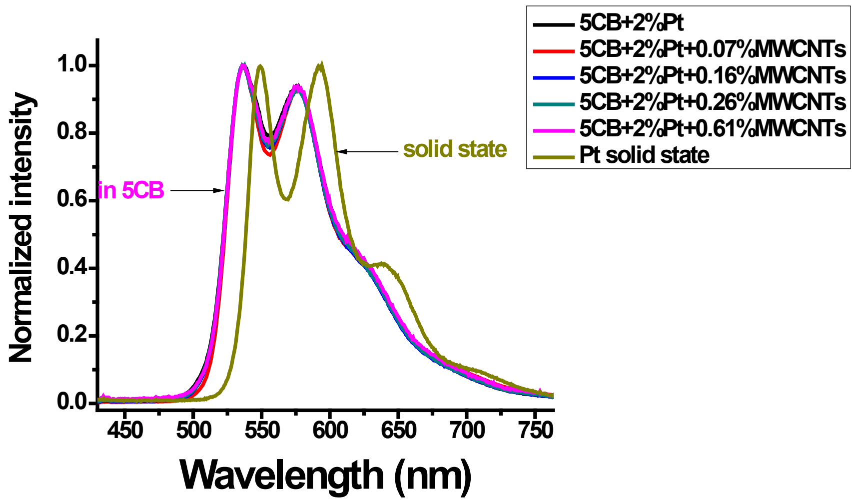
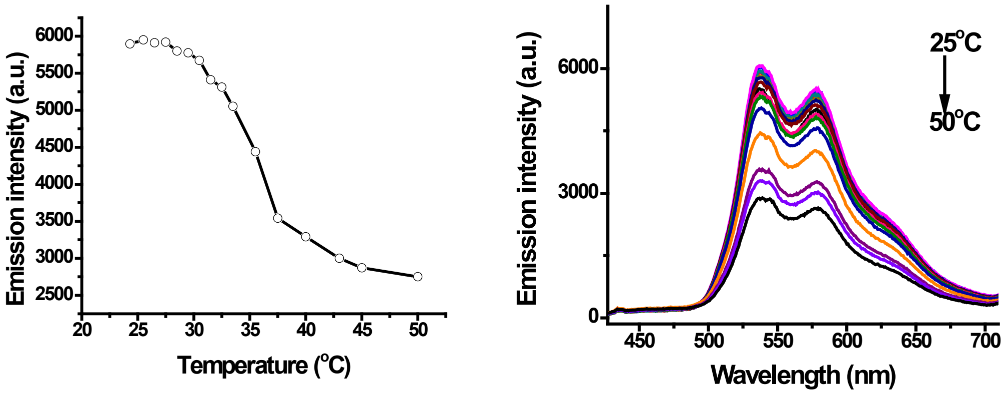


Fig. 4. Emission spectra of platinum(II) complex in solid state, 5CB and 5CB doped with MWCNTs.



(a) (b)

Fig. 5. Emission intensity vs temperature (a) and corresponding photoluminescence spectra (b) for 5CB+2%Pt sample measured in a planar cell.

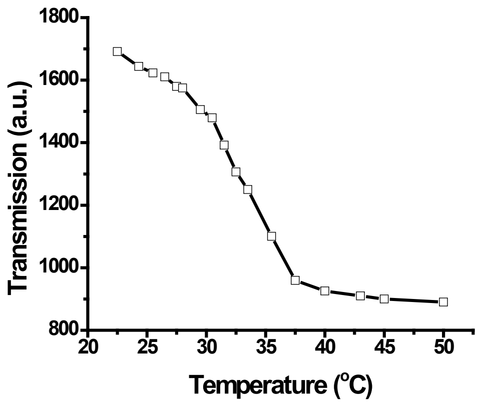


Fig. 6. Optical transmission vs temperature for 5CB+2%Pt sample measured in a planar cell with crossed polarizers.

The nematic to isotropic was also detected by measuring the optical transmission of a planar cell filled with the 5CB+2%Pt sample, within a temperature range of 22-50 ºC. Figure 6 depicts the relationship between temperature and optical transmission. As previously found for the emission intensity, a sudden decrease in optical transmission was observed in the vicinity of the nematic phase to isotropic transition. The T_{NI} value taken at the inflection point of the curve is ~ 34 ^{0}C which is slightly lower that the value detected by DSC and could be accounted to different heating rates used for the two experiments, 2 ºCmin^{-1} for optical transmission and 5 ºCmin^{-1} for DSC.

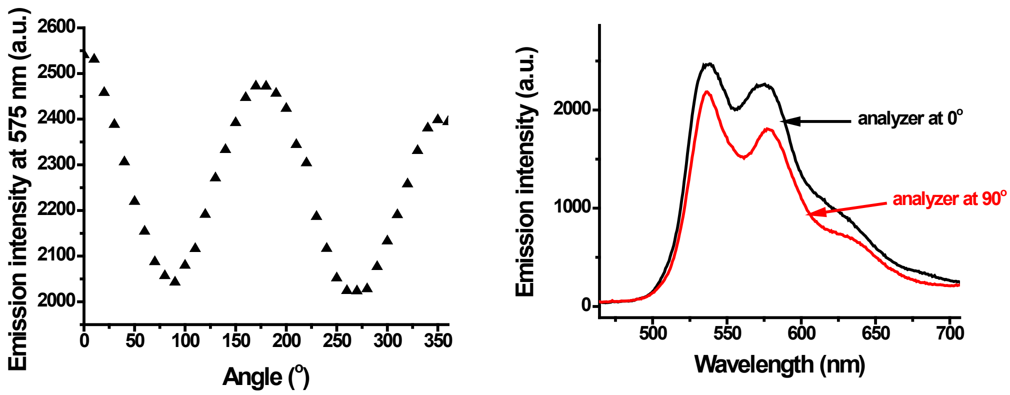
3.3. Emission anisotropy and order parameter for 5CB-Pt binary mixture

5CB is a nematic liquid crystal and, therefore, its rod-like molecules tend to align in a parallel manner, resulting in a significant orientational order over a large distance. The average orientation of the molecular long axes can be represented by a unit vector known as the *director*. However, the thermal fluctuations can induce significant deviations of individual molecules from the director. The degree of orientational order can be described by employing the order parameter *S*, which is defined in the following equation:

$$S = \frac{1}{2}\langle 3\cos^2\theta - 1 \rangle$$

where θ is the angle between the director and the long axis of the molecule. The order parameter of 5CB is 0.67, the reason why it can generate highly molecular dipole orientation and currently used to provide polarized light emission of various dyes dissolved in the LC matrix. [40, 41]

The emission anisotropy of the 5CB+2%Pt sample was recorded in a planar cell upon irradiation with unpolarized UV light. The emission spectra were measured after inserting a linear polarizer (analyzer) between the sample and the detector. Figure 7a shows the dependence of the emission polarization on the angle of the analyzer relative to the director of aligned LC. Figure 7b presents the steady-state photoluminescence spectra in the direction parallel ($\theta=0^o$) and perpendicular ($\theta=90^o$) to the director. Based on the analysis of Figure 7, it was seen that the two photoluminescence spectra have nearly identical shapes, regardless of the orientation of the analyzer. The dichroic ratio, denoted as P ($P=I_{II}/I_{\perp}$)[40], was estimated as 1.25 by integrating the emission intensity throughout a wavelength range of 400-700 nm. By using the following relationship $S=(P-1)/(P+2)$, the order parameter could be estimated as $S=0.08$. The value of order parameter for platinum(II) complex is very low compared to the values reported for other luminescent dyes doped in 5CB due to a large mismatch between the orientational orders of 5CB and platinum(II) complex suggesting a little parallel alignment of the platinum(II) dopant with the host molecules. This behavior could be explained by the large difference in size, molecular shape and polarity between the platinum(II) complex and 5CB. Obviously, the metal complex molecules do not prefer to align along the liquid crystal director given the square-planar geometry of the platinum(II) complex and the possible interactions of 5CB with the metal center. However, this behavior deserves a more comprehensive investigation in a subsequent study.



(a) (b)

Fig. 7. Modulation of the emission intensity at 575 nm (a) and the photoluminescence spectra (b) for 5CB+2%Pt with an analyzer angle from 0° (parallel to the LC director) to 90° (perpendicular to the LC director).

6. Conclusions

The effect of MWCNT concentration on the nematic to isotropic transition of 5CB and the emission of a Pt complex doped in 5CB were investigated and compared in this study. For this purpose, 5CB+2%Pt, 5CB+2%Pt+0.07% MWCNTs, 5CB+2%Pt+0.16% MWCNTs, 5CB+2%Pt+0.26% MWCNTs and 5CB+2%Pt+0.61% MWCNTs samples were prepared. According to POM images and emission measurements, all samples were observed to have the platinum(II) complex homogeneously dispersed in the LC matrix. The photoluminescence spectra do not exhibit any change due to the presence of MWCNTs in the samples. The nematic to isotropic phase transition was investigated by means of DSC, POM, emission spectroscopy and measurements of optical transmission in planar aligned cell. The values of T_{NI} obtained for Pt doped samples by emission and optical transmission measurements agree well with those obtained by DSC.

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