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To cite this article: Yosuke Iwai, Hiroshi Kouno, Yoshiaki Uchida & Norikazu Nishiyama (2015) Effects of Photonic Band Gap of Cholesteric Liquid Crystal on Chemiluminescence, Molecular Crystals and Liquid Crystals, 613:1, 163-166, DOI: [10.1080/15421406.2015.1032725](https://doi.org/10.1080/15421406.2015.1032725)

To link to this article: <http://dx.doi.org/10.1080/15421406.2015.1032725>



Published online: 06 Jul 2015.



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Effects of Photonic Band Gap of Cholesteric Liquid Crystal on Chemiluminescence

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We have fabricated glass cells filled with cholesteric liquid crystalline materials (CLC reflectors), which are mixtures of a nematic liquid crystalline mixture, ZLI-2293 (Merck), and a chiral dopant, MLC-6248 (Merck). We reported the enhancement of the maximum emission intensity of luminol reaction by the photonic band gap (PBG) of the CLC reflectors. Here, we report the effect of the relative position of PBG of the CLC reflectors to the emission spectra of luminol reaction on the enhancement of the maximum emission intensity.

Keywords Cholesteric liquid crystal; Chemiluminescence; Photonic band gap; Luminol reaction; CLC reflector

Introduction

Chemiluminescence is a light emission phenomenon that occurs as a result of a chemical reaction; the excitation energy is obtained not by any light absorption but by the chemical reaction. Therefore, the chemiluminescence has been used for detecting chemicals [1–5]. Luminol reaction is one of useful chemiluminescence reactions. Since the luminol reaction occurs by mixing luminol, catalytic metal ions and peroxides, it is commonly used for the detection of peroxides and metal ions. It is well known that the luminol reaction has been actually used to detect metal ions in human blood [1] and hydrogen peroxide (H₂O₂) as a marker of inflammation [2].

To improve the luminescence efficiency of luminol reaction, we focused on cholesteric liquid crystalline (CLC) materials, which operate as one-dimensional (1-D) photonic crystals due to its helical structure. We have recently reported the enhancement of emission intensity of luminol reaction when the reaction occurs between two glass cells filled with CLC materials (CLC reflectors) [6]. For a wide variety of applications of CLC materials to chemiluminescence sensors, the fine-tunable photonic band gap (PBG) of CLC by changing the composition ratio of nematic liquid crystalline (NLC) materials and chiral dopants should be investigated in more detail [7].

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Here, we report the PBG-dependence of the enhancement of emission intensity of luminol reaction using the CLC reflectors with different PBG wavelengths.

Experimental

Fabrication of the CLC reflectors

AL1254 (JSR) was spin-coated onto glass substrates at 5000 rpm for 20 s. After spin coating, the glass substrates were heated at 180°C for 1.5 h to remove residual solvents. After heating, the glass substrates were cooled to room temperature in a desiccator, and then the glass substrates were rubbed with velvet cloth five times. After rubbing, the glass substrates were cleaned with isopropyl alcohol (IPA: Wako) and heated at 90°C for 10 min to remove IPA. The glass substrates were assembled so that the rubbing directions on the top and bottom planes were opposite (antiparallel configuration). The glass cells were filled with a CLC mixture consisting of a nematic liquid crystalline mixture ZLI-2293 (Merck) and a chiral dopant MLC-6248 (Merck) by capillary action to give CLC reflectors.

Measurement of transmittance spectra of CLC reflectors and emission spectra of luminol reaction

Transmittance spectroscopy was carried out on an optical microscope (BX51: Olympus). The transmittance spectra of CLC reflectors were measured with a spectrometer (QE65Pro: Ocean Optics).

We pasted the CLC reflectors on two opposite sides of a plastic cell containing a luminol aqueous solution. 2.1×10^{-1} wt% luminol and 4.0×10^{-5} wt% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in polyethylenimine aqueous solution (pH 9.5), 100 μL of 3 wt% H_2O_2 aqueous solution was added to 1 mL of the luminol aqueous solution and we measured the emission spectra of the luminol reaction through the CLC reflector (**Fig. 1**). The emission spectra were measured with a spectrofluorometer (FP-6500: JASCO) and a fluorescence microplate reader (FMP-965: JASCO).

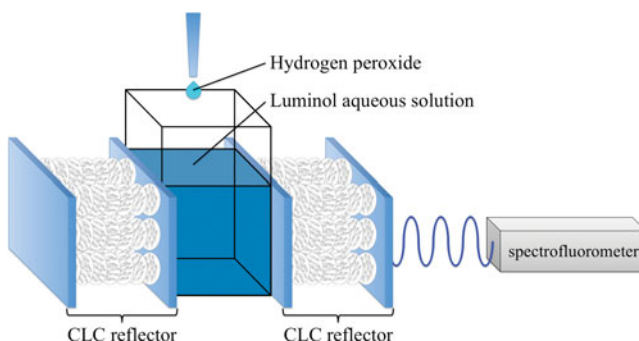


Figure 1. Experimental setup for the measurement of emission spectra of luminol reaction.

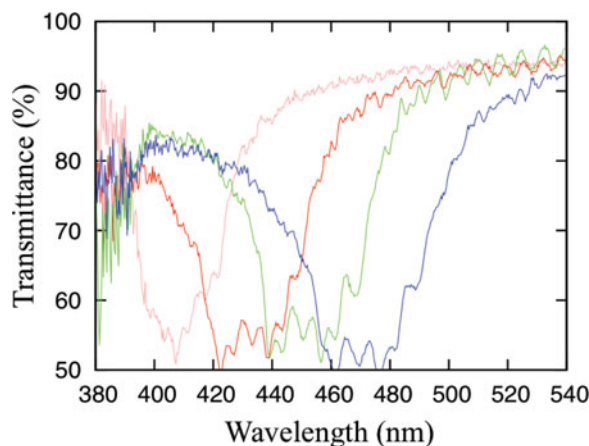


Figure 2. Transmission spectra of the CLC reflectors (a) pink line, (b) red line, (c) green line and (d) blue line.

Results and Discussion

First, we measured the transmission spectra for the CLC reflectors with various CLC materials. The PBG of the CLC reflectors depends on the composition of the CLC materials (**Fig. 2**). The CLC reflectors *a*, *b*, *c*, *d* with CLC materials containing 33.0 wt%, 30.5 wt%, 30.2 wt% and 29.9 wt% of MLC-6248 show PBGs between 397 – 422 nm, between 420 – 446 nm, between 440 – 467 nm and between 460 – 487 nm at 20°C, respectively.

The maximum emission intensity of luminol reaction is 425 nm in this reaction condition. We measured the emission spectra with empty glass cells and with the CLC reflectors (**Fig. 3**).

For all the CLC reflectors, the peak wavelength of the emission spectra shifted from 425 nm. The maximum emission intensities of luminol reaction with the CLC reflectors

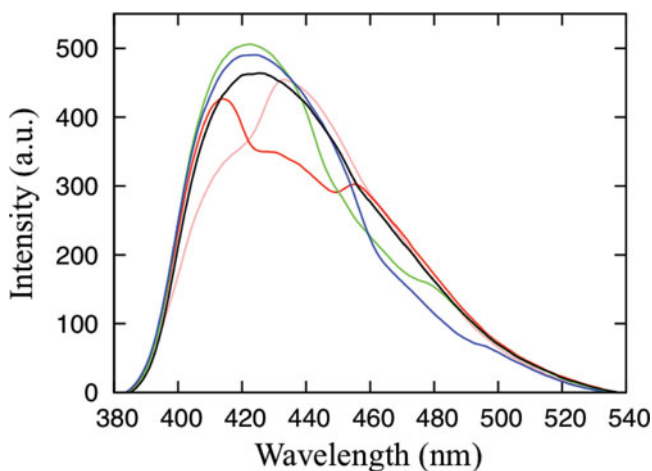


Figure 3. Emission spectra of luminol reaction with empty glass cells (black line) and with CLC reflectors (*a*; pink line, *b*; red line, *c*; green line and *d*; blue line).

a and *b* were smaller than that with empty glass cells (Fig. 3). Meanwhile, the maximum emission intensities of luminol reaction with CLC reflectors *c* and *d* were higher than that with empty glass cells (Fig. 3). These results suggest that the maximum emission wavelength of luminol reaction and the short wavelength edge of PBG of CLC materials should be closer for the enhancement of the peak intensity.

Conclusion

We measured the emission spectra of luminol reaction with CLC reflectors showing various PBG wavelengths. The experimental results indicate that the emission spectra depend on the relative position of the PBG wavelength. The highest peak of emission spectra was obtained with CLC reflectors with the short wavelength edge of PBG closest to the maximum emission wavelength of luminol reaction. We should design the chemiluminescence sensors using CLC materials with the PGB-dependence in mind.

Acknowledgments

The authors are very grateful to Merck & Co., Inc for providing ZLI-2293 and MLC-6248, JSR corporation for providing AL1254 and Prof. H. Umakoshi and Dr. K. Suga for their help with the use of the spectrofluorometer and fluorescence microplate reader. This work was supported in part by the Japan Science and Technology Agency (JST) 'Precursory Research for Embryonic Science and Technology (PRESTO)' for a project of 'Molecular technology and creation of new function'.

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