

	MOLECULAR CRYSTALS AND LIQUID CRYSTALS
	Volume 600, 2018
2017	KJF International Conference on Organic laterials for Electronics and Photonics (KJF-ICOMEP 2017): Part II
	GIST, Gwanglo, Korea August 30-September 2, 2017
	Gmant Editory

Molecular Crystals and Liquid Crystals

Taylor & Franci

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Xiaochuan Li, Yujie Han, Kyeongsu Min & Young-A Son (2018) Configuration of white light emission by courmarin and naphthalimide, Molecular Crystals and Liquid Crystals, 660:1, 10-16, DOI: 10.1080/15421406.2018.1452861

To link to this article: <u>https://doi.org/10.1080/15421406.2018.1452861</u>

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Published online: 02 May 2018.



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# Configuration of white light emission by courmarin and naphthalimide

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#### ABSTRACT

In this article, a dye with naphthalimide and coumarin was configured and was fully characterized. Its emission behavior was investigated in medium polar solvent. The emission behavior shows that there is no obvious energy transfer between naphthalimide and coumarin. Therefore, both the emission of naphthalimide and coumarin exhibit in the emission spectra, including blue and yellow part. The emission in film and solid shows different character. In film, single emission peak was observed. However, the solid emission covered a broad scope, including blue and yellow integrant. All the emission color was indicated by (Commission Internationale de L'Eclairage) CIE coordinates. The CIE coordinate of solid emission (0.29, 0.33) is approaching the ideal white light.

#### KEYWORDS

Coumarin; CIE; emission; naphthalimide; white light

# Introduction

Technology development significantly advances the quality of our life, which is based on the development of various special function materials. Additionally, higher requirements have been offered by the military service and special industry. Among various new types of materials, emissive molecules fascinate the physicists and chemists. Intensive effort and tremendous progress have been made toward this end and the spectra of fluorescent molecules overlap almost the whole visible region from blue to deep-red. Currently, typical emission molecules, such as coumarins, naphthalimide, bisindolylmalimide, perylenediimides, and rhodamine, have been systematically engineered toward various purposes [1–11]. A direct application is in signal translation and logic input/output. Therefore, robust fluorescent dyes with higher are desired for chemists, physicists and biochemists [12–15]. In addition, the fluorescent dyes are expected to have high quantum yield in solution and/or solid and structurally controllable emission wavelength. However, electronic excitation energy transfer (EET) is the unavoid element in configuration of multichromophoric systems [16–20]. Distance dependent is the typical character of EET mechanism; include Förster-type "Coulombic" interactions, Dexter-type

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exchange interactions, and other contributions to short-range coupling due to orbital overlap effects [21]. Fluorescence resonance energy transfer (FRET) is one of the typical EET models, which has succeeded applied in bio-sensors. In FRET cassette, spectral overlap between the donor emission and the acceptor absorptions is the key factor to efficiency of ET, which also set a threshold for the selection of emitters [22]. However, another ET mechanism (throughbond energy transfer, TBET) avoids the requirement of spectral overlap as that of the FRET. It affords the possibility of configuring multi-fluorescence-emitting single molecules by choosing suitable dye pairs [23, 24].

In this contribution, naphthalimide, green-yellow emitters, and coumarin, blue emitters were incorporated together. The two chromophores were linked by an *N*-containing bridge, which, to an extent, influence the energy transfer between naphthalimide and coumarin. By introduction alkyl substitution to the molecular framework, a mixed blue and yellow fluorescence could emit from this single molecule and obtain the white-light source. Compared to the multicomponent white-light sources, direct white light from a single component entity may be expected to avoid the drawbacks of combined emitters, thus giving rise to white light of higher quality. Therefore, configuring new molecular system that can emit white light is clearly of interest and importance.

#### **Experimental**

#### **General procedures and materials**

The solvents used in the reaction were carefully dried according to the standard procedure and stored over 4 Å molecular sieve. All the reagent-grade chemicals were purchased from Sigma-Aldrich CO. LLC. (South Korea) and used without further purification. Melting points were determined on a Mel-Temp<sup>®</sup> IA9200 digital melting point apparatus in a glass capillary and were uncorrected. All synthesized compounds were routinely characterized by TLC and <sup>1</sup>H NMR. TLC was performed on aluminum-backed silica gel plates (Merck DC. Alufolien Kieselgel 60 F254).

#### NMR spectroscopy and high resolution mass spectra (HRMS)

Nuclear magnetic resonance (NMR) spectra were recorded on a Brucker AM-400 spectrometer operating at frequencies of 400 MHz for proton in CDCl<sub>3</sub>. Proton chemical shifts ( $\delta$ ) are relative to tetramethylsilane (TMS,  $\delta = 0$ ) as internal standard and expressed in parts per million. Spin multiplicities are given as *s* (singlet), *d* (doublet), *t* (triplet), and *m* (multiplet) as well as *b* (broad). Coupling constants (*J*) are given in Hertz. The mass spectra measured on a LC-MS (Waters UPLC-TQD) mass spectrometer. High resolution mass spectra (HRMS) were measured on a Brucker micrOTOF II Focus instrument.

#### UV-Vis and emission spectra

The absorption spectra were measured with a PERSEE TU-1900 and an Agilent 8453 spectrophotometer. Emission spectra were measured with Shimadzu RF-5301PC fluorescence spectrophotometer. The solvents used in photochemical measurement were spectroscopic grade and were purified by distillation. The stock solution of compounds ( $2 \times 10^{-3}$  M) was



Scheme 1. Synthesis of BNC.

prepared and a fixed amount of these concentrated solutions were added to each experimental solution. All the experiments were done repeatedly, and reproducible results were obtained. Prior to the spectroscopic measurements, solutions were deoxygenated by bubbling nitrogen through them.

# **Synthesis**

The total synthesis of  $C_4$ -alkyl substituted naphthalimide-coumarin (**BNC**) is shown in Scheme 1. The synthesis started from 4-Br-1,8-naphthalimide (1) and *N*, *N*-diethyl salicylaldehyde (4), which are commercially available. 1 can be easily imidication when treated with *n*-octyl amine in refluxed ethanol [25, 26]. Subsequent substitution by nitrogen atom of hydrazine hydrate yielded *N*-allkyl-4-hydrazinyl-1,8-naphthalimide (3) [26]. Then it was condensed with 3-acetyl-7-diethylamino-coumarin (5), which was synthesized as described by known procedure, yielding the target  $C_4$ -alkyl substituted naphthalimide-coumarin (**BNC**), a bright powder.

# C<sub>4</sub>-alkyl substituted naphthalimide-coumarin (BNC)

*N*-allkyl-4-hydrazinyl-1,8-naphthalimide (**3**, 169.5 mg, 0.50 mmol) was charged into a dry flask with anhydrous ethanol (80 mL). Then, 3-acetyl-7-diethylamino-coumarin (**5**, 149.6 mg, 0.50 mmol) was added. The mixture was heated to reflux for 10 h. After the starting materials were fully reacted, as confirmed by TLC, the solvent was evaporated in vacuum. The residue was loaded to the column (silica gel 200–300 mesh) and eluted by mixed dichloromethane and ethyl acetate (50:1). Bright orange powder was obtained (226 mg, 84%).

Mp: 213–216°C; 1H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.68 (s, 1H), 8.58 (d, J = 7.2 Hz, 1H), 8.51 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.05 (s, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 6.50 (s, 1H), 3.36 (q, J = 5.6 Hz, 4H), 3.13 (t, J = 7.2 Hz, 2H), 2.13 (s, 3H), 1.53–1.61 (2H, m), 1.31–1.35 (2H, m), 0.93 (3H, t, J = 6.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  165.3, 162.8, 160.4, 156.0, 144.6, 135.0, 131.6, 131.4, 130.5, 129.9, 126.9, 125.8, 123.7, 119.8, 117.6, 113.1, 108.4, 96.1, 44.3, 41.4, 26.0, 14.7, 12.9. HRMS (ESI): Calcd. for C<sub>31</sub>H<sub>32</sub>N<sub>4</sub>O<sub>4</sub> [M+H<sup>+</sup>] 524.2424, found 524.2430.



Figure 1. Absorption spectra of **BNC** in selected solvents ( $1.0 \times 10^{-5}$  M).

# **Result and discussion**

The absorption behavior of **BNC** was investigated in selected organic solvents, such as toluene, chloroform, dioxane, and THF, because influence of the polar environment is more approach to the practical environment. The butyl substitution at naphthalimide provides appropriate solubility in most organic solvents. In contrast to its analogues, **BNC** also shows robust stability toward natural light, which was demonstrated by exposure to room light for several months with no color fading. Figure 1 shows the absorption contour of **BNC** in the selected solvents. In the selected medium polarity solvents, the absorption spectra are of similar shape with each other, indicating less solvatochromism. Obviously, the longest absorption band were located around 350–500 nm, with absorption peak around 450 nm and shoulder peak 400 nm. The maximum absorption at longer wavelength side could be ascribe to  $S_0 \rightarrow S_1$  transition with the bands on the high- and low-energy side corresponding to 0–1 and 0–0 vibration transition, respectively. According to the absorption range, it can be matched with the commercially available blue OLED (organic light-emitting diode) chip. **BNC** could absorb the UV light emitted by blue OLED chip with better efficiency.

The emission behavior is also investigated in the above selected solvents. Without the influence of strong polar environment, the emission band of **BNC** exhibits broad emission character, which includes blue (465 nm) and yellow (550 nm) two emission colors (Fig. 2). The mixture of blue and yellowish color could give an approximately white light. The two emission bands correspond to the typical emission region of coumarin (460 nm) and naphthalimide (548 nm). It is likely that the two fluorophores are simply mixed together, which indicates the



Figure 2. Emission spectra of **BNC** in selected solvents ( $1.0 \times 10^{-5}$  M).



Figure 3. CIE chromaticity diagram of the emissions of BNC in solutions.

energy transfer in the excited state is not sufficient. Therefore, appropriate molecular structure, together with the controllable intramolecular energy transfer, could realize the double emission as we designed for white light or approximate white light. The emission quantum yield in the selected solvents are determined to be 0.40 (chloroform), 0.41 (dioxane), 0.36 (THF), and 0.35 (toluene) with reference to quinine sulfate ( $\Phi = 0.55$ , 0.1N H<sub>2</sub>SO<sub>4</sub>) as a standard. The detailed emission color of **BNC** was demonstrated by CIE coordinates (Fig. 3). Obviously, CIE coordinates of the emission color do not distribute closely to the ideal white light coordinate (0.33, 0.33). It indicates that the proportion of blue part accounts higher in contrast to the yellow part. All the coordinates are corresponding to their emission in solution.

Due to the alkyl substitution to naphthalimide, it inhibits the molecules to form tight packing modes, avoiding the nonradiation energy loss. Therefore, **BNC** exhibits highly emissive character in film and solid state (Fig. 4). In film state, a single emission character was observed, which is different to the solution state. The CIE coordinate in film state also moves to the yellow-green region, indicating the naphthalimide emission character. It may relate with the polar environment of the polymer matrix. In addition, the polymer matrix could efficiently isolate the dye molecules in polymer lattices. It is similar to that in solution that the dye molecules were excited by absorbing energy via UV irradiation and transfer part of the



Figure 4. Emission spectra of BNC in film at 5 wt.% in polycarbonate. Inset: CIE coordinates of BNC in film.



Figure 5. Emission spectra of BNC in film at 5 wt.% in polycarbonate. Inset: CIE coordinates of BNC in solid.

energy to environment (solution or polymer). Obviously, the energy loss from dye molecules to polymer is higher than that from dye molecules to solvent molecules. Figure 5 shows the emission and CIE coordinate of **BNC** in solid state. In solid state, the effects of  $C_4$ -alkyl substitution, together with other unknown factor, inhibited the forming of over-tight packing efficiently between molecules and maintain the highly emissive character in solid powder. It is different from the energy loss of excited dye molecules in film (amorphous state) that the interaction between dye molecules were enhanced, which also enhanced the energy loss of excited dye molecularly, there is no efficient energy transfer between coumarin and naphthalimide and the emission band range from blue (420 nm) to red (650 nm). Among the emission region, the blue (460 nm) part and yellow part (560 nm) configuring the white light. However, the main emission of **BNC** in solid contains two emission peak 425 and 528 nm. It varies slightly away from the idea white light. The CIE coordinate (0.29, 0.33) accurately shows that the emission should be a blue-white emission definitely. Also, it leaves a scope in structure modification for configuring ideal white light.

# Conclusions

In summary, a newly designed dye molecule with two fluorophores was synthesized by incorporating coumarin and naphthalimide. It was fully characterized. The emission behavior shows there is no significant energy transfer between coumarin and naphthalimide. Therefore, **BNC** exhibits broad emission scope covering the blue and yellow region. The emission color in solution is approaching the ideal white light. In film state, the emission behavior is largely different from that of the solution, showing naphthalimide single emission character. In solid state, the  $C_4$ -alkyl substitution inhibits the over-tight packing and maintains its highly solid emissive character. The CIE coordinate of solid emission shows blue-white color character. Further structural modification based on **BNC** is still underway toward idea white light.

# Funding

This work was supported by the National Natural Science Foundation of China (21772034), and the Program for Innovative Research Team in University of Henan Province (15IRTSTHN003). This study was supported by the Basic Science Research Pro-gram through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (Grant No. NRF-2017R1E1A1A01074266).

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#### References

- [1] Sethna, S. M., & Shah, N. M. (1945). Chem. Rev., 36, 1.
- [2] Banerjee, S., Veale, E. B., Phelan, C. M., Murphy, S. A., Tocci, G. M., Gillespie, L. J., Frimannsson, D. O., Kelly, J. M., & Gunnlaugsson, T. (2013). *Chem. Soc. Rev.*, 42, 1601.
- [3] Oelgemoller, M., & Kramer, W. H. (2010). J. Photoch. Photobio. C, 11, 210.
- [4] Wu, W.-C., Yeh, H.-C., Chan, L.-H., & Chen, C.-T. (2002). Adv. Mater., 14, 1072.
- [5] Chen, C.-T. (2004). Chem. Mater., 16, 4389.
- [6] Li, X., Xu, Y., Wang, B., & Son, Y.-A. (2012). Tetrahedron Lett., 53, 1098.
- [7] Li, X., Zhao, N., Yu, L., & Son, Y.-A. (2015). Mol. Cryst. Liq. Cryst., 608, 273.
- [8] Li, X., & Son, Y.-A. (2015). J. Nanosci. Nanotechnol., 15, 5370.
- [9] Li, X., Zhang, J., & Son, Y.-A. (2015). J. Nanosci. Nanotechnol., 15, 5366.
- [10] Ramanan, C., Kim, C. H., Marks, T. J., & Wasielewski, M. R. (2014). J. Phys. Chem. C, 118, 16941.
- [11] Beija, M., Afonso, C. A. M., & Martinho, J. M. G. (2009). Chem. Soc. Rev., 38, 2410.
- [12] Loudet, A., & Gurgess, K. (2007). Chem. Rev., 107, 4891.
- [13] Ziessel, R., Ulrich, G., & Harriman, A. (2007). New. J. Chem., 31, 496.
- [14] Ulrich, G., Ziessel, R., & Harriman, A. (2008). Angew. Chem. Int. Ed., 47, 1184.
- [15] Li, X., Ji, G., J, J.-M., & Son, Y.-A. (2016). Mol. Cryst. Liq. Cryst., 636, 159.
- [16] Scholes, G. D. (2003). Annu. Rev. Phys. Chem., 54, 57.
- [17] Li, X., Zhu, K., Li, Y., Kim, H., & Son, Y.-A. (2013). Mol. Cryst. Liq. Cryst., 584, 18.
- [18] Li, X., & Son, Y.-A. (2014). Mol. Cryst. Liq. Cryst., 601, 182.
- [19] Parkinson, P., Kamonsutthipaijit, N., Anderson, H. L., & Herz, L. M. (2016). ACS Nano, 10, 5933.
- [20] Okada, D., Nakamura, T., Braam, D., Dao, T. D., Ishii, S., Nagao, T., Lorke, A., Nabeshima, T., & Yamamoto, Y. (2016). ACS Nano, 10, 7058.
- [21] Hsu, C.-P. (2009). Acc. Chem. Res., 42, 509.
- [22] Yu, H., Xiao, Y., Guo, H., & Qian, X. (2011). Chem. -Eur. J., 17, 3179.
- [23] Reddy G, U., Ali, H. A., Taye, A. F. N., Chattopadhyay, S., & Das, A. (2015). Org. Lett., 17, 5532.
- [24] Belušáková, S., Lang, K., & Bujdák, J. (2015). J. Phys. Chem. C, 119, 21784.
- [25] Li, X., Zhang, Y., Zhao, N., & Son, Y.-A. (2014). Mol. Cryst. Liq. Cryst., 600, 163.
- [26] Wang, J., Xu, Z., Zhao, Y., Qiao, W., & Li, Z. (2007). Dyes Pig., 74, 103.