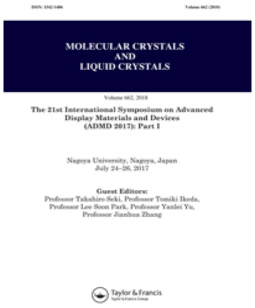

MOLECULAR CRYSTALS
AND
LIQUID CRYSTALS

Volume 662, 2018

The 21st International Symposium on Advanced
Display Materials and Devices
(ADMD 2017): Part I

Nagoya University, Nagoya, Japan
July 24–26, 2017

Guest Editors:
Professor Takahiro Seki, Professor Tomiki Ikeda,
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Molecular Crystals and Liquid Crystals

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

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To cite this article: Yun Liu, Xiaochuan Li, Kyeong Su Min & Young-A Son (2018) Emission behavior of naphthalimide-coumarin cassette, Molecular Crystals and Liquid Crystals, 662:1, 139-146, DOI: 10.1080/15421406.2018.1466533

To link to this article: https://doi.org/10.1080/15421406.2018.1466533

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2018, VOL. 662, 139–146
https://doi.org/10.1080/15421406.2018.1466533

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Emission behavior of naphthalimide-coumarin cassette

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ABSTRACT

In this contribution, a dye (C_8-alkyl substituted Naphthalimide-Coumarin, CNC) with naphthalimide and coumarin incorporated together with *-NHN* = bridge unit. The compound was fully characterized by NMR and HRMS spectroscopic techniques. Highly emissive character was investigated in detail in various polar environments. The emission maximum varied from 430 to 470 nm. In polycarbonate film, CNC is also highly emissive with 560 nm emission peak. While in sold, the emission maximum was further shifted to 580 nm due to the more tightly packing mode than that in film. The C_8-alkyl substitution enhances the solubility of CNC and also contributes most to its solid emission.

KEYWORDS

C_8-alkyl; coumarin; highly emissive; naphthalimide; solid emission

1. Introduction

Nowadays, a fluorophore with larger Stoke's shift is of great beneficial to the DNA sequencing detection, in vivo optical imaging system, various sensors, smart logic devices, and artificial light-harvesting apparatus, which has been attractive the interests of chemists, physicists, and biochemists [1–11]. Configuring an energy transfer cassette is an effective way to enlarger the gap of the excitation and emission wavelength. Self-absorption could be avoided effectively by the enlarged Stoke's shift. In addition, the fluorescent dyes are expected to have high quantum yields in solution and/or in solid and structurally controllable emission wavelength. Therefore, electronic excitation energy transfer (EET) is one of the key factors in configuration of multichromophoric systems [12–16]. Distance between dye pairs is the key parameter in EET mechanism; include Förster-type "Coulombic" interactions, Dexter-type exchange interactions, and other contributions to short-range coupling due to orbital overlap effects [17]. Fluorescence resonance energy transfer (FRET) is another typical EET models, which has succeeded applied in bio-sensors. In FRET cassette, spectral overlap between the donor's emission and the acceptor's absorptions is the key factor to efficiency of ET, which also set a threshold for the selection of emitters [18]. However, another ET mechanism (through-bond energy transfer, TBET) avoids the requirement of spectral overlap as that of the FRET.

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It affords the possibility of configuring larger Stoke's shift by choosing suitable dye pairs [19, 20].

Developing novel fluorescent molecules with larger Stoke's shift are of important in material and biological application. TBET and FRET are useful tools to reach this end. Herein, two highly emissive fluorephore, coumarin and naphthalimide, are selected and incorporated together with a bridge. It provides great potential in sensor application and optical device fabrication. The interaction occurred the bridge unit may influence the effect of ET, once the electronic states of this bridge were altered between coumarin and naphthalimide. Uncovering the principle behind them is the key issue to understanding the physical properties of the energy transfer cassette.

2. Experiment

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./Alfa Aesar-A Johnson Matthey Company (South Korea) and used without further purification. Melting points were determined on a Mel-Temp® IA9200 digital melting point apparatus in a glass capillary and were uncorrected. All synthesized compounds were routinely characterized by TLC and ^{1}H NMR. TLC was performed on aluminum-backed silica gel plates (Merck DC. Alufolien Kieselgel 60 F254).

^{1}H/^{13}CNMR, IR, and high resolution mass spectroscopy

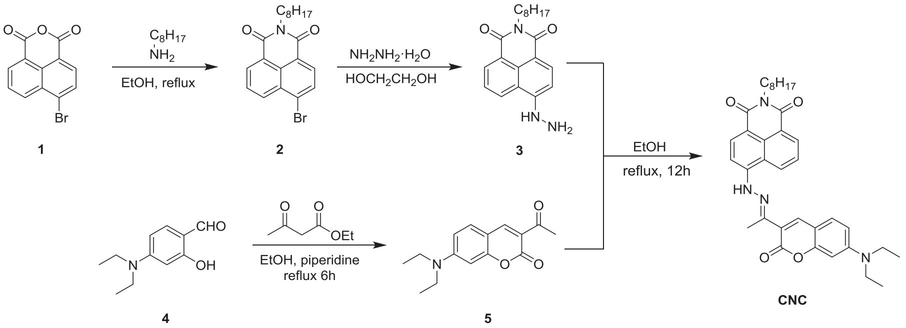
^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-400 spectrometer operating at frequencies of 400 MHz for proton 100 MHz for carbon in $CDCl_3$. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, $\delta = 0$) as internal standard and expressed in 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. Infrared (IR) spectra were run in KBr on an FTS-175C IR spectrometer ($\upsilon_{\max}$ in cm^{-1}). High resolution mass spectra (HRMS) were measured on a Bruker microOTOF 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 (2×10^{-3} M) was prepared in CH_3CN, 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_8-alkyl substituted Naphthalimide-Coumarin (**CNC**) is shown in Scheme 1. The synthesis is started from 4-Br-1,8-naphthalimide (**1**) and *N*, *N*-diethyl



Scheme 1. Synthetic routes of C_8-alkyl substituted naphthalimide-coumarin (CNC).

salicylaldehyde (**4**), which are commercially available. **1** can be easily iimidication when treated with *n*-octyl amine in refluxed Ethanol [21, 22]. Subsequent substitution by nitrogen atom of hydrazine hydrate yielded *N*-allkyl-4-hydrazinyl-1,8-naphthalimide (**3**) [22]. Then it was condensed with 3-acetyl-7-diethylaminocoumarin (**5**), which was synthesized as described by known procedure, yielding the target C_8-alkyl substituted Naphthalimide-Coumarin (C**NC**), a bright orange powder.

C_8-alkyl substituted naphthalimide-coumarin (CNC)

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**, 129.5 mg, 0.50 mmol) was added. The mixture was heated to reflux for 10 h. After the starting materials were full 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 (246.5 mg, 85%).

Mp: 167–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (1H, *b*, –N*H*), 8.59 (1H, *d*, $J = 7.2$ Hz, $Ar_{nap}H$), 8.53 (1H, *d*, $J = 8.4$ Hz, $Ar_{nap}H$), 8.21 (1H, *d*, $J = 8.0$ Hz, $Ar_{nap}H$), 8.07 (1H, *s*, $Ar_{cou}H$), 7.76 (1H, *d*, $J = 8.4$ Hz, $Ar_{nap}H$), 7.69 (1H, *t*, $J = 7.8$ Hz, $Ar_{nap}H$), 7.39 (1H, *d*, $J = 8.8$ Hz, $Ar_{cou}H$), 6.64 (1H, *d*, $J = 8.0$ Hz, $Ar_{cou}H$), 6.49 (1H, *s*, $Ar_{cou}H$), 4.18–4.10 (2H, m, $-CH_2-$), 3.45 (4H, *q*, $J = 7.2$ Hz, $-(CH_2)_2-$), 2.54 (3H, *s*, $-CH_3$), 1.72 (2H, *m*, $-CH_2-$), 1.41 (2H, *m*, $-CH_2-$), 1.29–1.20 (14H, *m*, $-(CH_2)_4-(CH_3)_2$), 0.86 (3H, t, $J = 6.8$ Hz, $-CH_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.4, 163.9, 161.3, 156.9, 144.9, 133.6, 131.1, 130.2, 130.1, 129.5, 125.6, 125.4, 123.2, 119.2, 113.5, 110.6, 109.7, 108.2, 96.7, 45.2, 40.3, 31.8, 29.4, 29.3, 28.2, 27.2, 22.7, 14.7, 14.1, 12.5. HRMS (ESI): $[M+H]^+$ $C_{35}H_{41}N_4O_4$ requires 581.3128, found $[M+H]^+$ 581.3074.

3. Results and discussion

The absorption behavior of **CNC** was investigated in different organic solvents, including hexane, toluene, chloroform, dioxane, tetrahydrofuran (THF), acetonitrile, methanol, *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) (Fig. 1). Due to the introduction of C_8-alkyl, **CNC** exhibit excellent solubility in the tested solvents. In addition, robust stability of **CNC** toward light was observed with no color fading, even if several months' exposure to room light. The fundamental absorption/emission maximum, coefficients, quantum yields, etc are collected in Table 1. In medium polarity solvents (from toluene to acetonitrile), the absorption contour indicates weak solvatochromism (Fig. 1). Similar shapes were observed with two main absorption peaks around 430 and 530 nm. With the

Table 1. Optical data of **CNC** in several solvents.

	UV-Vis		Fluorescence			
Solvent	λ_{abs} (nm)	$\log \varepsilon_{max}$	λ_{em} (nm)	Φ_F	FWHM (nm)	Stokes shift (nm)
hexane	416/535	4.49/3.54	430	0.09	58	14
toluene	425/537	4.56/4.40	454	0.42	46	29
chloroform	432/536	4.65/4.45	465	0.40	44	33
dioxane	420/533	4.58/4.38	460	0.51	47	40
THF	425/533	4.59/4.43	465	0.08	48	40
acetonitrile	428/528	4.53/4.28	470	0.09	62	42
methanol	432/530	4.58/2.34	—	—	—	—
DMF	432/533	4.56/4.40	—	—	—	—
DMSO	436/533	4.56/4.04	—	—	—	—

[a] Full width at half maximum is abbreviated as FWHM.

solvent polarity increasing further, the longest maximum absorption peaks was weakened. Especially, the 530 nm absorption was significantly weakened in hexane. Medium solvent polarity contributes more to the longest maximum absorption. $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transition could be assigned to the 530 and 430 nm, respectively. Obviously, the former are slightly outweigh the latter. Absorption longer than 580 nm is almost optically transparent.

Notably, **CNC** is highly emissive in the studied organic media. Detailed emission parameters are listed in Table 1. The emission spectra in different solvents are presented in Fig. 2. In different polarity solvents, the emission intensity of **CNC** is largely different. It was significantly quenched in methanol, DMF, and DMSO. While in dioxane, chloroform, toluene, and THF, **CNC** is highly emissive with the emission peaks ranging from 454 to 465 nm, which leads to the blue fluorescence color. Mainly, the 0–0 transition of vibronic progress contributes most to the blue emission, which suggests that the geometry of the ground state and the excited are quite similar. Obviously, the emission band of coumarin is observed (430 nm). Only in dioxane, a trace of 550 nm emission could be found. When the naphthalimide was excited, the coumarin emitted its typical fluorescence emission, indicating no energy transfer from to coumarin naphthalimide. Even if there is perfect spectra overlap between the donor emission (coumarin) and the acceptor absorption (naphthalimide), the energy transfer is significantly influenced by the structure factor (C_8-alkyl substituted) and

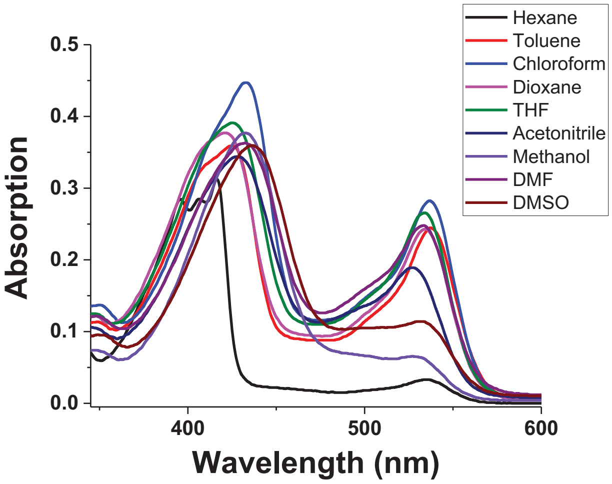


Figure 1. Absorption spectra of **CNC** in several solvents (1.0×10^{-5} M).

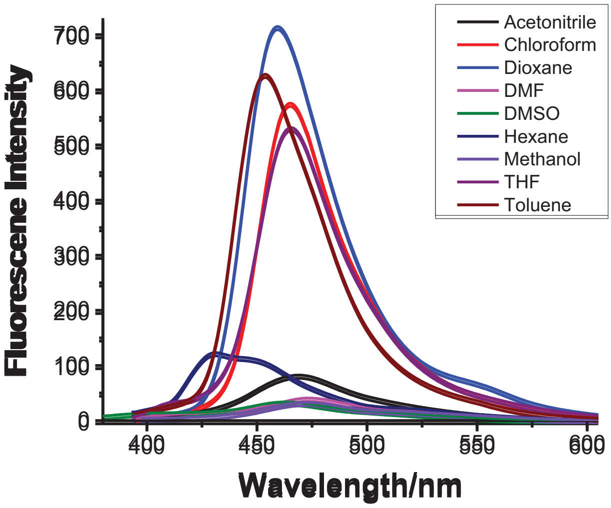


Figure 2. Emission spectra of **CNC** in various solvents (1.0 × 10^{-5} M).

solvent polarity. Slightly positive solvatochromism showing in Fig. 1 indicates that the value of the dipole moment in the excited electronic state (μ_e) is larger than that in the ground state (μ_g). Therefore, the dipole-dipole interaction of the excited molecules in the polar environment is stronger than that of the excited molecules in non-polar environment. *N*, *N*-diethylamino attaching to coumarin strongly donated electron to coumarin, but it is partially inhibited by C_8-alkyl substitution at naphthalimide. The electron density of naphthalimide will be enhanced and it will be stabilized by polar environment in the excited state. Thus, the emission of naphthalimide was quenched significantly. The bridge unit ($-NHN=$) is also a highly electron density part, which is easy influenced by C_8-alkyl. Stabilization in the excited state of naphthalimide by polar solvent could lead to very low emission quantum yield.

It should be noted that **CNC** is also highly emissive in film with 5 wt.% in polycarbonate, as shown in Fig. 3. In comparison with the emission behavior in solution, the emission maximum in the film state shows significant bathochromic shift toward longer wavelength (560 nm). In comparison to the emission of naphthalimide, about 20 nm shifts could be calculated due to the tighter packing in polymer matrix. According to the narrow emission band (FWHM = 66 nm), it can be deduced that the monomers emission contributes mostly to the film emission. In addition, polycarbonate could provide a polar matrix lattice, which effectively isolates the dye molecules in polymer lattices. Similar to the emission in solution, the excited dye molecules in polymer matrix dissipate part of the energy to polymer and to lower energy state (S_1). Both the polar environment and the irregular tight packing in polycarbonate matrix contribute to the emission bathochromic shift. In the solid powder state, the emission maximum was further red-shift to 580 nm, indicating tighter packing than that of film. Additionally, the emission in solid powder was broadened, with the full width at half maximum reaching to 80 nm (broader than that of polycarbonate film 66 nm). The solid powder is composed by micro crystals, in which the dye molecules were packed regularly than that it in polymer matrix. Therefore, the excited dye molecules in solid state could dissipate more energy to adjacent dye molecule easily, and then return to the ground state, emitting longer wavelength fluorescence. Finally, the energy loss of excited dye molecules was enhanced in solid state in contrast to that in polycarbonate film, leading to a further red-shift of fluorescence emission. On top of that the FWHM of solid emission was broadened furtherly to 76 nm due to the more

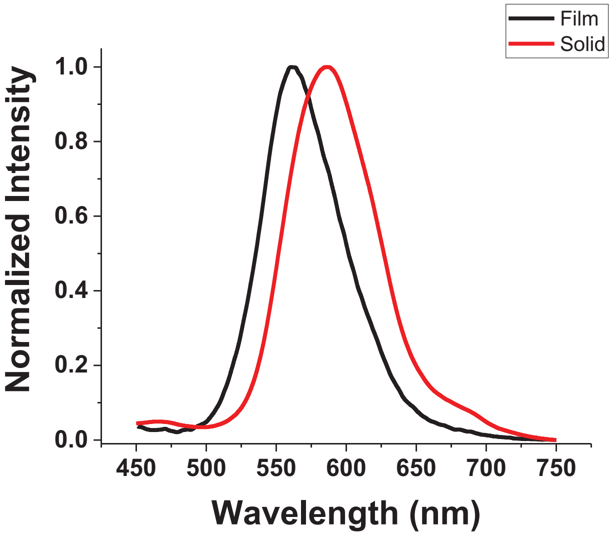


Figure 3. Emission spectra of **CNC** in film at 5 wt.% in polycarbonate. Emission and excitation slit widths were set to be 3 nm.

complicated interactions between dye molecules in solid state than that in film between dye molecules and amorphous polymer chains. More importantly, the highly emissive character in polycarbonate film is attractive for **CNC**, which makes it a potential dopant emitter in host materials. And the introduction of C_8-alkyl in naphthalimide also avoids higher regular packing in solid, which contributes mainly to its solid emission. Generally, the solid emission will be quenched in solid state due to the highly regular π-π stacking, and enhance nonradiation energy transition. Without the long chain effect, quenched emission has been demonstrated, for example C_3-alkyl substitution [23].

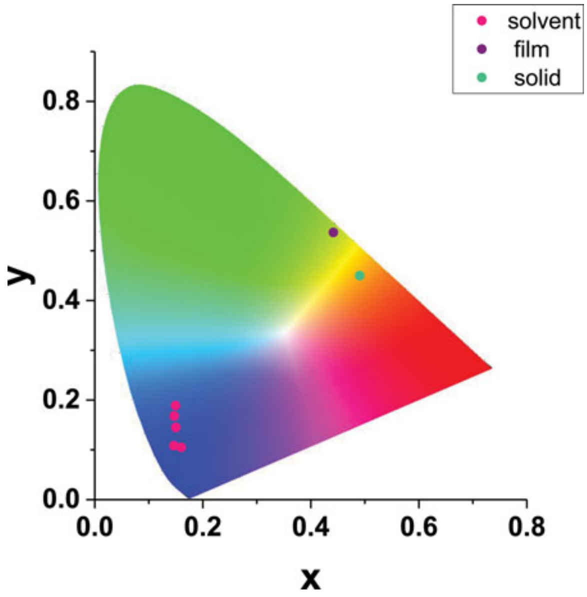


Figure 4. CIE 1931 chromaticity diagram of the emissions of **CNC** in solutions, film, and solid.

The emission color changes in solution and film were characterized by Commission Internationale de L'Eclairage (CIE) coordinates (Fig. 4). In solution state, the emission color of **CNC** scattered in blue region. In hexane and toluene, the CIE coordinates distributed in deep blue region. With the polarity increasing (chloroform, THF, dioxane), the CIE coordinates shifts slightly to light blue region, which is in agreement with their emission profiles in solution. Notably, the CIE coordinate of **CNC** in film state is observed and moves to green region. In solid state, the emission color moved further to orange region due to the tight molecular packing.

4. Conclusions

In conclusion, a new dye with two fluorophores was configured by naphthalimide and coumarin with fully characterization. The absorption and emission behavior of **CNC** in various solvents, in film, and in solid state were studied. A long alkyl chain was introduced to naphthalimide unit, enhancing the solubility in organic medium. **CNC** is highly emissive in medium nonpolar solvents. Particularly, dioxane induces most emissive character with the emission maximum at 460 nm. In polycarbonate film, **CNC** is also highly emissive with emission peak shifting to green region (560 nm). Due to the tightly molecular packing in solid, the emission maximum was further shifted to the orange region (580 nm). The emission color of **CNC** in solution/film/solid powder was characterized by CIE coordinates in detail. It indicates that the excitation and excited state of **CNC** is easy to be interfered by the polar conditions induced by the solvents or polymer matrix. Our efforts toward the application of TPN in device fabrication and biological purpose are currently underway.

Funding

This work was supported by the National Natural Science Foundation of China (21272060, 21772034), PCSIRT (grant no. IRT1061), and the Program for Innovative Research Team in University of Henan Province (15IRTSTHN003). This study was also supported by the National Research Foundation of Korea (NRF) (Grant No. NRF-2017R1E1A1A01074266).

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