

Column Chromatography: A Facile and Inexpensive Procedure to Purify the Red Dopant DCJ Applied for OLEDs

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Abstract

DCJ, one of the DCM derivatives, has been used as a laser dye and a red emitter or a red dopant for OLED devices in recent decade. 4-(dicyanomethylene)-2-methyl-6-(julolidyl-9-enyl)-4*H*-pyran (DCJ) containing julolidine group has been synthesized for use as a red fluorescent dye molecule in organic light-emitting diodes (OLEDs). In this paper, we reported a facile, simple and inexpensive procedure of purification of DCJ without necessity of HPLC analysis. The maximum absorption, emission, quantum efficiency are increasing in DCJ with the electron-donating of julolidine group.

Keywords: Purification, Column Chromatography, Absorption, Emission, Quantum Efficiency

1. Introduction

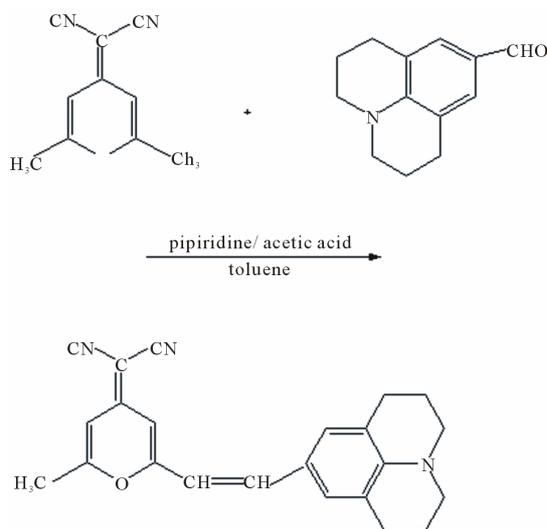
In recent years, the study of synthesis, structure and chemical properties of organic light emitting diodes (OLED) electronic materials has become one of the foremost topics in chemistry and physics [1-3]. Since the introduction of first multi-layer high efficiency thin-film OLEDs devices by Tang and Van Slyke [4], OLEDs have attracted considerable interests for flat-panel display applications. For the flat panel and full color display, it is necessary to have a set of green, blue and red emitters with sufficiently high luminous efficiency and proper chromaticity. At present time, the OLED materials with blue and green emission have been well developed; however, the red OLED materials require more investigation [5]. In 1989, C. W. Tang in Kodak has improved the efficiency and synthesis of DCM compounds as red dopants [6]. Then Shim *et al.* determined the julolidyl substituted aniline group in the DCM molecule as DCJ for organic electro-luminescent devices. It is wellknown that the pyran containing dyes such as DCM and DCJ (4-(dicyanomethylene)-2-methyl-6-(julolidyl-9-enyl)-4*H*-pyran) have been widely used as red emitters OLEDs. Maximum emission and absorption

wavelength increases with the electron-donating or the electron-withdrawing abilities of different substituents in the aniline as electro-donating group or the pyran as electron-withdrawing group of DCM derivatives [7]. The enhanced electron donating ability of julolidine originated from the increased communications between the lone electron pair on the nitrogen atom and phenyl π system with the help of two six member locking rings [8]. The symmetrical electron acceptor procedure, 4-(dicyanomethylene)-2,6-dimethyl-4*H*-pyran, 1, (**Scheme 1**) was used to prepare DCJ.

However, under the normal Knoevenagel reaction conditions, the bis-condensed byproduct is inevitably in the precursor, which is quite difficult to be separated from the DCJ product and tends to quench the fluorescence of DCJ, 1 [9,10].

Therefore, in this paper to eliminate the bis-condensed by product, we purpose a simple way for complete purification of DCJ dye.

Purification was carried out by Column chromatography instead of HPLC analysis with variety ratio of solvents. This method is very simple and needs no expensive equipments in comparison with HPLC analysis.



Scheme 1. Synthesis of DCJ.

2. Experimental

2.1. Materials and Apparatus

The chemicals were obtained from Merck Chemical Company and Aldrich Chemical Company and were used without further purification. Melting point was analyzed with an electro thermal melting point apparatus. The ^1H NMR spectrum was obtained on FT-NMR (500.3 MHz) Bruker spectrometer. The chemical shifts are expressed in δ ppm using TMS as an internal standard. Mass spectra were recorded on a FINNIGAN-MATT 8430 mass spectrometer operating at an ionization potential of 20 eV. Absorption and fluorescence spectra in solutions were recorded using an Avantes Avaspec-2048 UV-Vis spectrophotometer. The fluorescence quantum yield of the compound was measured by thermal lens effect method. Chromatography columns were prepared from Merck silica gel 60 mesh.

2.2. Synthesis of 4-Dicyanomethylene-2,6-dimethyl-4H-pyran

A mixture of malonitrile (1 mmol), 2,6-dimethyl-4H-pyran-4-one (1 mmol) and acetic anhydride (0.5 cm^3) was refluxed for 1.5 h. The unreacted acetic acid was removed and the residue was washed with 50 ml. of boiling water and was collected to give soft brown material. Recrystallization from boiling heptane produced a brown powder [11].

2.3. Synthesis of DCJ

A solution of (0.8 mmol) 9-julolidine carboxaldehyde, 2

(1 mmol) 4-dicyanomethylene-2,6-dimethyl-4H-pyran, 1 shown in **Scheme 1** and 13 drops of piperidine and 15 drops of HOAc in 14 cm^3 of toluene were refluxed under argon gas for 18 hours. On cooling, the precipitated dye was filtered (yield: 65%). The product was purified by column chromatography using n-hexane-ethyl acetate (6:1) as eluent. The yield of separated bis-condensed from the DCJ, 3 is 99% and the result was contaminated with 1% of bis-condensed byproduct.

The chemical structure of DCJ was characterized as follow:

Dark green crystals (from 6:1 hexane-ethyl acetate), MS, m/z (%): 356 (M^+ , 100), ^1H NMR (500 MHz, DMSO): δ 1.88 (4H, m, $2\text{CH}_2\text{CH}_2\text{N}$), 2.4 (3H, s, CH_3), 3.2 (4H, t, $J = 5.6\text{ Hz}$, 2Ar-CH_2), 2.7 (4H, t, $J = 6.1\text{ Hz}$, $2\text{CH}_2\text{N}$), 6.1 (2H, s, 2ArH), 6.5 (1H, s, 1pyran-H), 6.6 (1H, s, 1pyran-H), 6.9 (1H, d, $J = 15.8\text{ Hz}$, $\text{CH} = \text{CH}$), 7.3 (1H, d, $J = 15.8\text{ Hz}$, $\text{CH} = \text{CH}$), 7.1 (2H, s, Ar).

3. Results and Discussion

DCJ is intermolecular charge-transfer compound, which its emission wavelength has been affected by the relative electron-donating abilities of the donor group. In this study, DCJ containing julolidine as an electron donor has been synthesized and its purification procedure was reported Section 2. Maximum fluorescence and maximum absorption wavelength and quantum efficiency of DCJ dye (630.6 nm, 486.6 nm, 65%) increased in comparison with DCM dye (619.4 nm, 459.1 nm, 46.5%) [10].

The concentration of dye solutions was $2.8 \times 10^4\text{ M/l}$ in ethyl acetate solvent. Normalized fluorescence and absorption spectra are shown in **Figure 1**. Unwanted bis-condensed byproducts was to substitute the methyl group with julolidine group. The intermediate of one way to circumvent the difficulties in synthesis and subsequent purification of DCJ for removing the the new red dopants

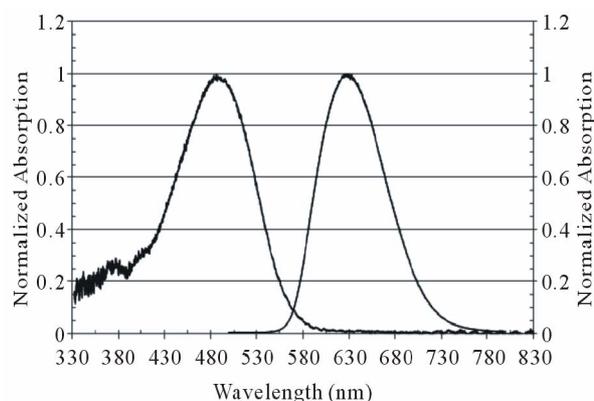


Figure 1. UV-Vis normalized absorption (left curve) and normalized fluorescence (right curve) spectrum of DCJ dye.

has a symmetrical structure, the byproducts are the results of the reaction of two symmetrical methyls, in two sides of intermediate molecule with julolidine carboxaldehyde. This byproduct tends to decrease the fluorescence efficiency of DCJ, counteracting the effect of reduction of concentration quenching, which only has a very weak fluorescence in the near infra-red region of the visible spectrum.

In this work, we reported a facile, simple and inexpensive method for purification of DCJ. It was shown the product can be purified by column chromatography using hexane-ethyl acetate as an eluent. At first stage, recrystallization method seems to be a useful way for byproducts separation. By using this procedure the ratio of unwanted byproducts was decreased but not separated completely. At second stage column chromatography improved our aim for complete purification. Initially, a more polar ratio of solvents was used. Thin layer chromatography showed that unwanted byproducts weren't separated completely. To improve the purification, we used a less polar ratio of solvents, then TLC showed unwanted DCJ dye byproducts were almost removed. Finally, we used a non-polar ratio of solvents (6:1 n-hexane-ethyl acetate) and TLC showed that unwanted byproducts were completely separated. The ^1H NMR spectrum of DCJ exhibit characteristic signals with appropriate chemical shifts which showed that purification by column chromatography was successful.

As expected, both the absorption and fluorescence spectra of DCJ (**Figure 1**) exhibited an increase in the electron donating julolidine group relative to that of DCM [10]. In other words, DCJ indicated larger quantum efficiency than DCM.

4. Conclusions

One of the DCM type red light emitter, DCJ, was synthesized and successfully purified by a facile and inexpensive method. Purification was carried out by column chromatography instead of HPLC analysis with different ratio of solvents. We used n-hexane-ethyl acetate (6:1) as an eluent for separation of unwanted DCJ byproduct. Maximum fluorescence, maximum absorption wavelength and quantum efficiency of DCJ increased in comparison to DCM, because of the existence of the electron donating julolidine group.

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