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Theoretical investigation of electro-luminescent properties in red emission DCM, DCJ, RED and DAD derivatives

Bo-Cheng Wang[a,*], Hsien-Ren Liao[a], Wen-Hao Chen[a], Yu-Ma Chou[b], Jyi-Tyan Yeh[c], Jian-Chuang Chang[c]

[a]*Department of Chemistry, Tamkang University, Tamsui, Taipei 25137, Taiwan, ROC*
[b]*Department of Physics, Chinese Culture University, Taipei 110, Taiwan, ROC*
[c]*Materials Research Laboratory, ITRI, Hsinchiu 310, Taiwan, ROC*

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Abstract

During last decade, the DCM derivatives have been used as a laser dye and a red emitter or a red dopant for OLED devices. A series of unsymmetrical DCM, DCJ, and RED as well as symmetrical DAD derivatives of DCM have been recently synthesized and proposed for the commercial applications. It is found experimentally that the optical properties of these materials are determined by their electronic structure. However, no reliable and accurate computational method exists to predict the spectral properties currently. In this paper, we used the semiempirical AM1 and ab initio DFT methods to generate the optimized structures of DCM, DCJ, RED and DAD derivatives. Using the semiempirical ZINDO and ab intio TD-DFT methods, we generated the excitation and emission energies for these derivatives. According to the calculation results, the red shift in the excitation wavelength is in the order RED > DCJ > DCM, the maximum absorption and emission are increasingly red-shifted in DCM derivatives with the electron-donating of the different substituents in the aniline as electron-donating group or with the electron-withdrawing abilities of different substituents in the pyran as electron-withdrawing group.

Keywords: Electron-withdrawing; Electro-luminescent; DCM

1. Introduction

During the past decade, the study of the 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]. 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 [4]. At present time, the OLED materials with blue and green emission have been developed very well. However, the red OLED materials are significantly behind those for the other two colors [5]. 4-(Dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)-styryl]-4H-pyran (DCM) is a very efficient laser dye, with emission at the color region from orange to red (wavelength from 570 to 620 nm), which was used for a tunable light source in a broad spectral region [6,7]. In 1989, C.W. Tang in Kodak has improved the efficiency, chromaticity, and synthesis of the DCM compounds as red dopants [8]. Valeur et al. [9] proposed general procedures for the synthesis of DCM and mono-substituted DCM derivatives. Then, Shim et al. [10,11] determined the julolidyl substituted aniline group in the DCM molecule as DCJ derivatives for organic electro-luminescent devices. Symmetrical derivatives of DCM have been synthesized and their nonlinear optical properties have been confirmed by Moylan's group [12]. Furthermore, the new red dopants with a chromene instead of pyran as the electron acceptor group have been proposed by Lee [13]; these red dopants were denoted as RED. Till now, the organic syntheses and investigation of physical properties of DCM derivatives have been proposed widely

* Corresponding author. Fax: +886 2 622 8458.
E-mail address: bcw@mail.tku.edu.tw (B.-C. Wang).

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[8–10]. Although much research work has been done in the organic synthesis of DCM derivatives, very few papers on the theoretical and quantum mechanics calculations of these derivatives can be found in the literature. In 1992, Marguet used the semiempirical INDO method to predict the intra-molecular charge transfer and *trans–cis* isomerization of the DCM compound [14]. Recently, the femtosecond fluorescence up-conversion technique and TD-DFT calculations have been used by Diau [15] to investigate the dynamics of DCM. For the theoretical investigation of the chromophore compounds, recently, we used the semiempirical AM1 and ab initio TD-DFT calculation methods to determine the absorption and emission spectra for the derivatives of maleimide, 1,4-distyrylbenzene and pyrene. A comparison with the experimental data shows that the calculation results in the related electronic materials are very accurate and reliable [16,17].

Theoretically, most of the chromophore activity in the OLED materials is due to a $\pi^* \leftarrow \pi$ transition electronically. In this paper, the semiempirical AM1 and ab initio DFT methods have been used to optimize the ground and the excited states structure of DCM, DCJ, RED and DAD derivatives. Then, we used the semiempirical ZINDO and ab initio TD-DFT methods to determine the absorption and emission energies based on the geometry from the semiempirical AM1 calculation (both for the ground and the excited states) and to generate the various spectral properties of these derivatives including excitation and emission energies and relative intensities. The 0–0 absorption and downward fluorescence transition have been considered in this calculation.

2. Theoretical calculations

In this study, we classify the DCM derivatives according to different substituents in the parent DCM compound, as the series of DCM, DCJ, RED for the unsymmetrical DCM derivatives and DAD for the symmetrical DCM derivatives. Fig. 1 shows the molecular structures of DCM and its derivatives. The structure of DCM includes arylidene with a dimethylamino group linked to two cyano groups by a conjugated bridge at either end of the DCM. The molecule in which dimethyl-phenyl-amine in DCM is replaced by julolidyl moiety is denoted as DCJ. Fig. 2 shows the molecular structures of a series of DCJ derivatives. The molecule in which pyran moiety is substituted by a chromene is denoted as RED; the molecular structures of a series of RED derivatives are depicted in Fig. 3. DCD compounds (Fig. 4) are symmetrical DCM derivatives, which contain two substituents in the pyran ring and exhibit C_2 symmetry.

In this work, the geometries of DCM, DCJ, RED and DCD derivatives in the ground state were fully optimized at the semiempirical AM1 and ab initio (DFT/B3LYP/6-31G*) levels of theory. The electronic transition properties, which include the maximum excitation wavelength (λ_{max}^{abs}) and intensities (oscillator strengths, f), were obtained by the semiempirical ZINDO method and time-dependent density functional theory (TD-DFT), respectively. Consequently, the semiempirical AM1 method (the keyword is 'EXCITED' with *.DAT input file, which bases on the optimized structure of AM1 calculation) was used to obtain geometric structures of the excited state (S_1) for these

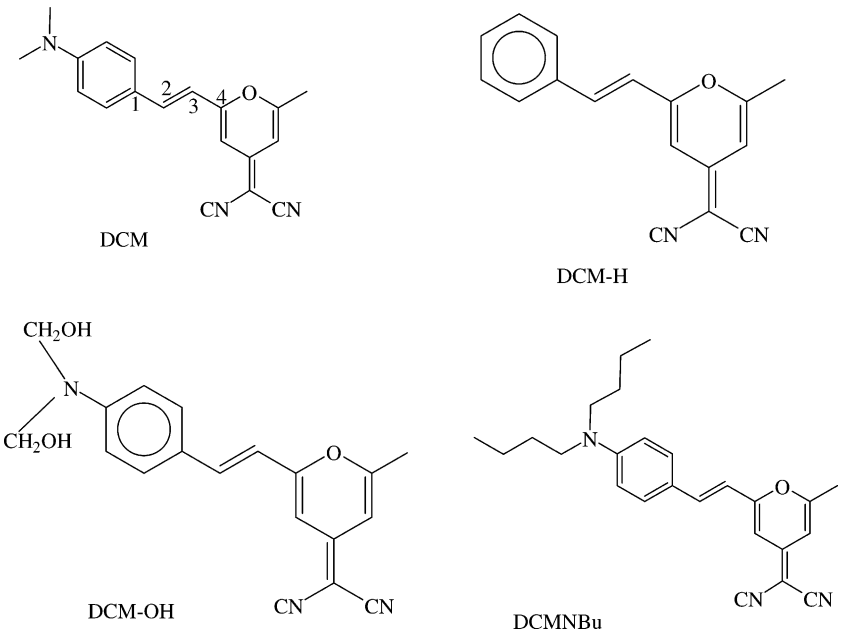

Fig. 1. Geometrical structures of DCM derivatives.