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2D–π–A type pyran-based dye derivatives: Photophysical properties related to intramolecular charge transfer and their electroluminescence application

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Abstract

Five different types of 2D–π–A (vinylcyanoacetate)pyran derivatives, each having two donor (2D) and one acceptor (A) groups showed significantly large Stokes shifts. Their fluorescence bands shifted to longer wavelengths with an increase in solvent dielectric constant. The π-conjugated moiety, such as a carbazolyl group, as an electron donor did not impart red-emission saturation. A locked ring structure of the electron donor group led to narrowing of the full width at half maximum (fwhm) and to increased dipole moment in the ground state; in addition, bulky donor groups resulted in molecular stability and restrained electronic perturbation on the excited state. An EL device based on the dyes displayed bright and saturated red light with a high luminance of about 2000 cd/m^2 at a current density of 160 mA/cm^2 at 16 V.

Keywords: Fluorescence; Pyran-based dye; Electron donor; Electron acceptor; Charge transfer; Electroluminescence

1. Introduction

Electron donor–π-conjugate–electron acceptor (D–π–A) compounds are interesting due to their nonlinear optical properties, which are highly sensitive to changes in the external environment such as polarity and pH of media, due to their intrinsic intramolecular charge transfer (ICT) character [1]. Among many of the related compounds synthesized up to date, the pyran-based dyes have been intensively developed for applications using as photo- (PL) and electroluminescent (EL) materials in the fields of dye laser [2], sensor [1e,3], dye-sensitized solar cell [4], and organic light-emitting device (OLED) [5]. The 4-(dicyanomethylene)-2-methyl-6-(*p*(dimethylamino)styryl)-4*H*-pyran (DCM) is the representative compound, which produces the ultrafast process of ICT [6]. As well, the excited-state dipole moment (26.3 D) is higher than that in the ground state (6.1 D) [7]. Thus, DCM is highly charge-separated at a photoexcited state and shows a remarkably large Stokes shift leading to red-emission color saturation. Fundamental studies on the photophysical properties of its derivatives are still crucial for the exploration of new functions and applications in dye chemistry.

Since Tang and VanSlyke reported that a double layered organic EL device consisting of a hole injection layer and an emitting layer exhibited a luminance over 1000 cd/m^2 at a relatively low driving voltage of 10 V, there have been extensive studies

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on layered organic EL devices with the aim of achieving high brightness and full color emission [8,5c]. In order to obtain the high performance organic EL, organic materials are required to have good thermal stability and the ability to form amorphous thin films. There are two methods for tuning the color emitted from organic EL devices: an appropriate selection of the emitting materials with bright luminescence of desired colors or doping dyes into the host material. The former method is the most feasible for producing blue-light-emitting EL devices [9], and the latter is useful for the fabrication of the bright red-light-emitting organic EL devices [10]. DCM derivatives are well-known as low molecular weight red-emitting materials, which can be synthesized by a relatively simple method [11].

In this work, we synthesized five different types of 2D–π–A pyran-based dyes, (vinylcyanoacetate)pyran derivatives, having two donors (2D) and one acceptor (A) groups, as shown in Chart 1. Their fundamental, photophysical properties related to ICT character were investigated in various dilute solutions. Furthermore, EL property of one of these compounds was described in detail.

2. Experimental section

*2.1. Synthesis of ethyl 2-cyano-2-(2,6-dimethyl-4H-pyran-4-ylidene)acetate, **8** [12]*

A mixture of 2,6-dimethylpyran-4-pyrone, **6** (25 mmol, 3.1 g), ethyl cyanoacetate, **7** (25 mmol, 2.7 ml), and acetic acid (12.5 ml) was refluxed for 6 h. The pale yellow solid obtained was filtered, washed with methanol, and recrystallized from methanol several times.

Yield: 43%, m.p. 184–186 °C; mass (*m/z*) 219 (M^+); ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81 (s, 1H), 6.59 (s, 1H), 4.14 (m, 2H), 2.33 (s, 6H), 1.22 (t, $J = 7.52$, 3H); Anal. Cald. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.61; H, 6.12; N, 6.20%.

*2.2. Synthesis of (vinylcyanoacetate) pyran derivatives, **1–5***

A solution of 2-cyano-2-(2,6-dimethyl-4*H*-pyran-4-ylidene)acetate, **8** (4.6 mmol, 1 g), 4-dimethylamino benzaldehyde **1′** (10.1 mmol, 1.5 g) and piperidine (0.45 ml) in 1-propane (30 ml) was refluxed for 8 h using a Dean–Stark trap. The reaction solution was cooled to room temperature, and the solid product was isolated and washed well with 1-propanol, and dried. The crude product was recrystallized from methanol several times. Compounds **2–5** were obtained by a similar procedure using **2′**, **3′**, **4′** and **5′**, respectively.

Compound **1**: Yield: 23%, m.p. 254 °C; mass (*m/z*) 481 (M^+); ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98 (s, 1H), 7.45 (d, $J = 9.04$, 4H), 7.42 (d, $J = 4.04$, 1H), 7.38 (d, $J = 4.00$, 1H), 6.70 (d, $J = 9.04$, 4H), 6.65 (s, 1H), 6.55 (m, 2H), 4.25 (m, 2H), 3.05 (s, 12H), 1.35 (t, $J = 7.04$, 3H); Anal. Cald. for $C_{30}H_{31}N_3O_3$: C, 74.82; H, 6.49; N, 8.73. Found: C, 74.07; H, 6.50; N, 8.65%.

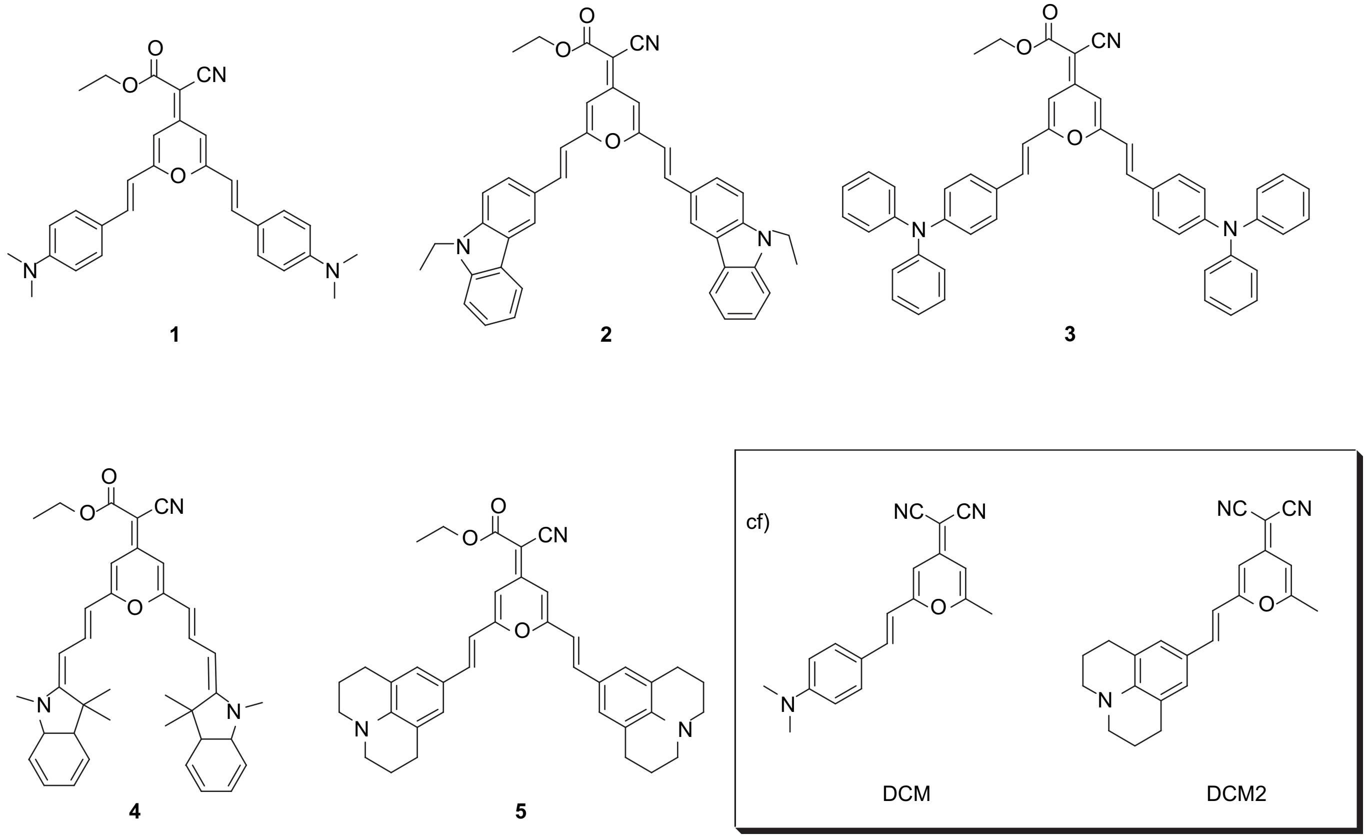

Chart 1. Chemical structures of (vinylcyanoacetate)pyran derivatives, **1–5**.