A novel n-type red luminescent material for organic light-emitting diodes

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A novel red luminescent material *N,N*-bis{4-[2-(4-dicyanomethylene-6-methyl-4*H*-pyran-2-yl)ethylene]phenyl}aniline (BDCM) with two (4-dicyanomethylene)-4*H*-pyran electron-acceptor moieties and a triphenylamine electron-donor moiety for application in organic light-emitting diodes (OLEDs) was synthesized. The resultant compound has a sterically well-hindered structure and a high fluorescence yield. The photoluminescence (PL) of this compound in solution and solid film and the electroluminescence (EL) have been studied. Based on its intense sterically hindered structure, the pure BDCM film prepared shows a bright red PL emission. The three-layered EL device with the structure ITO/CuPc/DPPhP/BDCM/Mg:Ag has a turn-on voltage of less than 4 V, which suggests that BDCM has an excellent electron injection property. A bright luminance of 582 cd m^{-2} is obtained for the device at 19 V.

Introduction

Since the first high-performance red OLEDs were obtained by doping a guest red luminescent dye into an Alq$_3$ host matrix in 1989 by Tang *et al.*,[1] there have been intense research activities in developing new organic red dopants, such as dicyanomethylene-containing red dopants,[1–7] rare earth metal complexes[8,9] and porphyrin compounds.[10,11] The advantages of the doping method include easy color tuning, higher luminance, improved efficiency, and superior stability of the device. For these dopants some criteria such as high fluorescence quantum yield and proper chromaticity are required.[3] However, most of the red dopants developed so far suffer from severe concentration quenching, although many efforts have been made to overcome it.[1,2] Furthermore, the interactions between the guest dopants and host matrix (*e.g.* energy transfer and electron transfer) often make the resultant emission complicated. For example, when the energy transfer between a Alq$_3$ host matrix and red dopant is not complete, the fluorescence of Alq$_3$ cannot be quenched completely, which results in impure red emission of the device.[6,10] This problem can be avoided by using host red emitting materials, which are used as the emitting layer as well as hole or electron transport layer. To do so, some requirements for red emitting materials should be met, including the absence of concentration quenching; perfect electron or hole injection and transport properties as well as high fluorescence quantum yield in the red region.

In this paper, the design and synthesis of a new red luminescent material, *N,N*-bis{4-[2-(4-dicyanomethylene-6-methyl-4*H*-pyran-2-yl)ethenyl]phenyl}aniline (BDCM), containing two (4-dicyanomethylene)-4*H*-pyran electron-acceptor moieties and a triphenylamine electron-donor moiety is reported, which can meet the requirements mentioned above for host red emitting materials. The photoluminescence (PL) of BDCM in solution and solid film and the electroluminescence (EL) performance in solid film have been studied. As expected, the rigidity and non-planar structure of the triphenylamine moiety offers BDCM a sterically well-hindered feature, and consequently an excellent pure red emission is obtained for the pure BDCM film due to significantly diminished concentration

quenching. Further, the presence of two electron-acceptor moieties increases the electron affinity (EA) of BDCM,[12,13] and as a result, grants the BDCM efficient electron injection and transport abilities. The combination of the above advantages, as the result of incorporating triphenylaniline and two (4-dicyanomethylene)-4*H*-pyran moieties into one molecule make it possible for BDCM to serve as a host red emitter.

Experimental section

Measurements

^{1}H NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz), except for DCM-TPA which was measured on a Varian WM-300 spectrometer (300 MHz). Mass Spectra (MS) were measured on a Finnigan GC-MS 4021 C spectrophotometer. Elemental analyses were measured by the Flash EA 1112 method. Infrared spectra of BDCM were taken as KBr pellets using a BIO-RAD FTS-165 FT-IR spectrometer. The melting points of compounds are uncorrected. Absorption and fluorescence spectra in solutions were recorded using a Shimadzu UV-1601PC UV-Vis spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. The fluorescence quantum yields of the compounds were estimated by using DCM1 as the calibration standard at a similar concentration. Single-layer thin solid films were fabricated by casting dye solutions (5 × 10^{-3} M) in chloroform at the surface of quartz glasses.

Materials

The structures and synthetic steps of 1,3-diphenyl-5-(9-phenanthryl)-2-pyrazoline (DPPhP), 4-(dicyanomethylene)-6-methyl-2-{2-[(4-dimethylamino)phenyl]ethenyl}-4*H*-pyran (DCM1), 4-(dicyanomethylene)-6-methyl-2-[2-(julolidin-9-yl)ethenyl]-4*H*-pyran (DCM2), 4-(dicyanomethylene)-6-methyl-2-{2-[(4-diphenylamino)phenyl]ethenyl}-4*H*-pyran (DCM-TPA), and *N,N*-bis{4-[2-(4-dicyanomethylene-6-methyl-4*H*-pyran-2-yl)ethenyl]phenyl}aniline (BDCM) are shown in Chart 1, Schemes 1[14] and 2,[15] respectively. The intermediates **I**,[16] **II**,[17] and **III**[18]
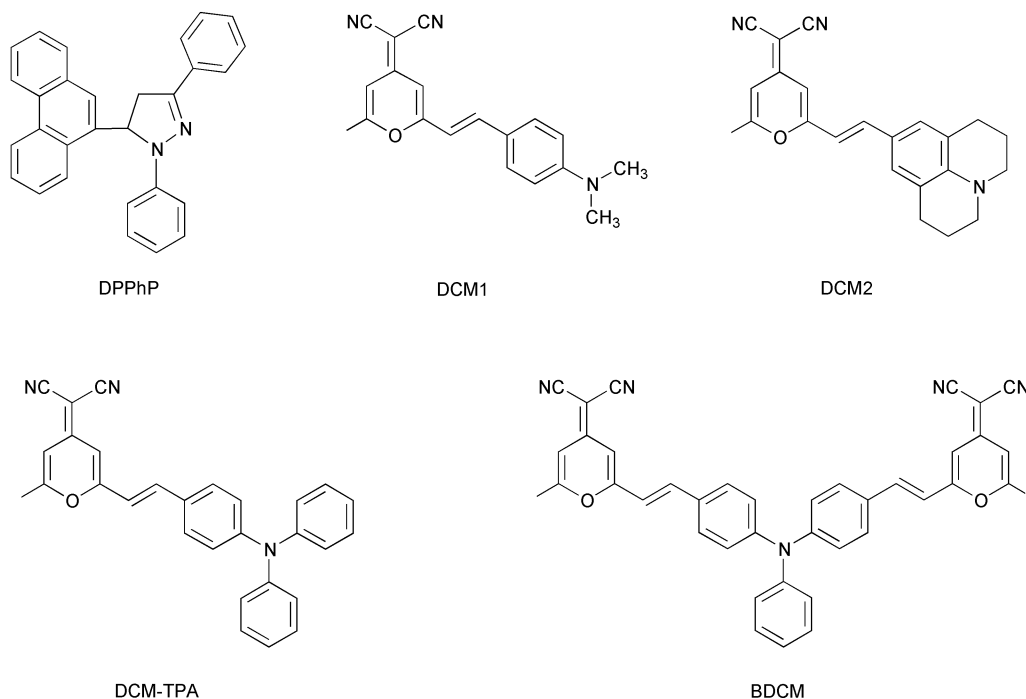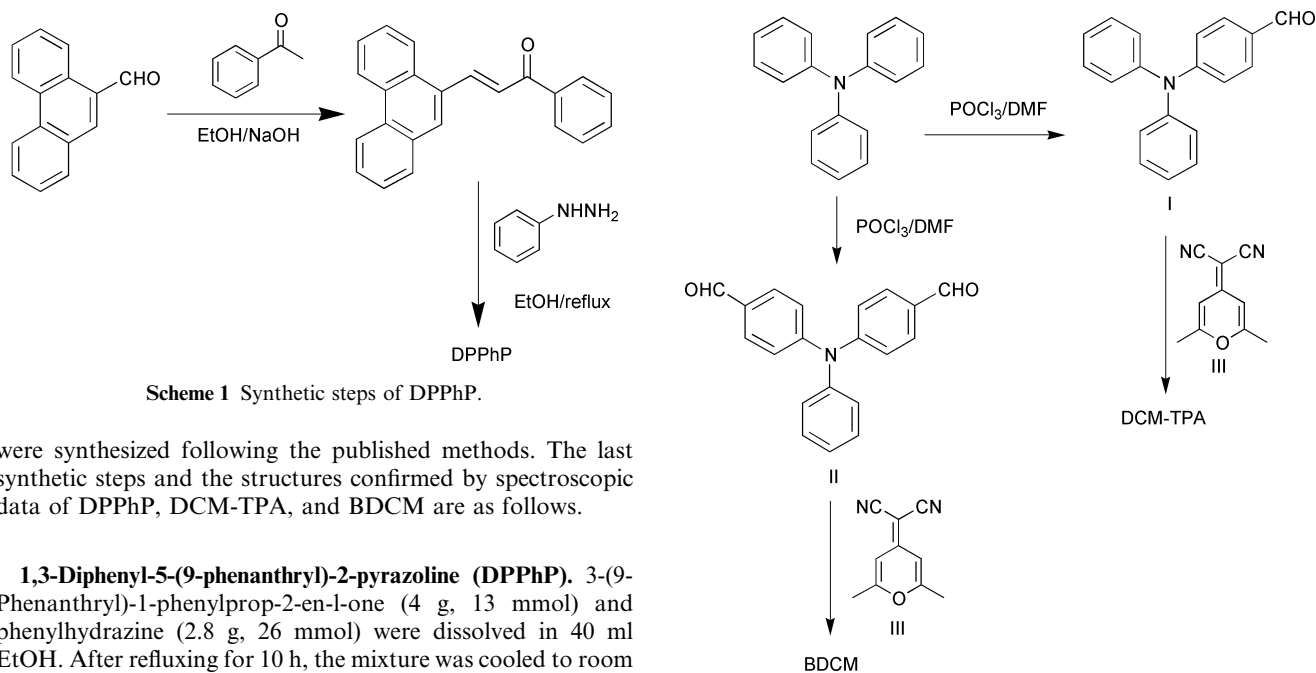
Chart 1 Molecular structures of DPPhP, DCM1, DCM2, DCM-TPA, and BDCM.

Scheme 1 Synthetic steps of DPPhP.

Scheme 2 Synthetic steps of DCM-TAP and BDCM.

were synthesized following the published methods. The last synthetic steps and the structures confirmed by spectroscopic data of DPPhP, DCM-TPA, and BDCM are as follows.

1,3-Diphenyl-5-(9-phenanthryl)-2-pyrazoline (DPPhP). 3-(9-Phenanthryl)-1-phenylprop-2-en-l-one (4 g, 13 mmol) and phenylhydrazine (2.8 g, 26 mmol) were dissolved in 40 ml EtOH. After refluxing for 10 h, the mixture was cooled to room temperature and the solid product was filtered and washed with EtOH to give 4.2 g crude product. It was recrystallized from THF–EtOH to give colorless DPPhP crystals (3.73 g, 72%). mp 245–247 °C; ^{1}H NMR: (CDCl$_3$, 400 MHz) δ: 3.2 (m, 1H), 4.1 (m, 1H), 5.9 (m, 1H), 6.8 (t, 1H, J = 6.9 Hz), 7.12–7.21 (m, 5H); 7.32 (d, 1H, J = 7.2 Hz), 7.38 (t, 2H, J = 7.6 Hz), 7.54 (t, 1H, J = 7.5 Hz), 7.63 (t, 1H, J = 7.1 Hz), 7.65–7.76 (m, 5H), 8.15–8.17 (m, 1H), 8.67 (d, 1H, J = 7.2 Hz), 8.83 (m, 1H); MS m/z (%): 398 (M$^+$, 33.68), 306 (21.97), 221 (30.13), 91 (100).

4-(Dicyanomethylene)-6-methyl-2-{2-[(4-diphenylamino)phenyl]-ethenyl}-4H-pyran (DCM-TPA). 4-Dicyanomethylene-2,6-dimethyl-4H-pyran (**III**, 180 mg, 1.05 mmol), 4-diphenylamino-benzaldehyde (**I**, 240 mg, 0.88 mmol), and piperidine (0.1 ml) were dissolved in 5 ml of dry acetonitrile. After refluxing for 10 h, the solvent was removed under vacuum; the dark red product was washed with ethanol and purified by column chromatography on silica using 4 : 1 (v/v) hexane : chloroform

as the eluent. Yield (210 mg, 56%). mp 271–273 °C; ^{1}H NMR: (CDCl$_3$, 300 MHz) δ: 2.42(s, 3H), 6.51 (d, 1H), 6.55–6.61 (d, 1H), 6.64 (s, 1H), 7.00–7.42 (m, 15H); MS m/z (%): 427 (M$^+$, 100), 383 (4.63), 412 (25.37).

N,N-Bis{4-[2-(4-dicyanomethylene-6-methyl-4H-pyran-2-yl)-ethenyl]phenyl}aniline (BDCM). 4-Dicyanomethylene-2,6-dimethyl-4H-pyran (**III**, 180 mg, 1.05 mmol), 4-diphenylamino-benzaldehyde (**I**, 100 mg, 0.33 mmol), and piperidine (0.1 ml) were dissolved in 5 ml of dry acetonitrile. After refluxing for 2 h, the solvent was removed under vacuum; the dark red product was washed with ethanol and purified by thin layer chromatography on silica by eluting with 8 : 1 (v/v) chloroform : hexane. The product eluted as the second fluorescence band. Yield (70 mg, 35%). mp 289–292 °C; ^{1}H NMR: (CDCl$_3$, 400 MHz) δ:

2.41 (s, 6H), 6.54 (d, 2H, J = 1.11 Hz), 6.57–6.62 (d, 2H, J = 15.94 Hz), 6.66 (d, 2H, J = 1.91 Hz), 7.11–7.13 (d, 4H, J = 8.61 Hz), 7.16–7.18 (d, 2H, J = 7.51 Hz), 7.21 (t, 1H, J = 7.5 Hz), 7.35 (t, 2H, J = 6.61 Hz), 7.36–7.41 (d, 2H, J = 15.62 Hz), 7.42–7.45 (d, 4H, J = 8.65 Hz); MS: m/z (%): 609 (M$^+$), 332 (2.05), 71 (100); Anal. Calcd for $C_{40}H_{27}N_5O_2$: C: 78.80, H: 4.46, N: 11.49. Found: C: 78.48, H: 4.57, N: 11.27%; IR (KBr): 698, 840, 926, 976, 1177, 1210, 1289, 1328, 1416, 1499, 1556, 1592, 1653, 2210.

Preparation of EL device and EL testing

The EL device fabricated in this work has a configuration of ITO/CuPc (50 nm)/DPPhP (50 nm)/BDCM (50 nm)/Mg:Ag. Copper phthalocyanine (CuPc) was used as the hole-injection layer, and DPPhP was used as the hole-transport layer. BDCM was used as the emission layer as well as electron injection and transport layer. ITO-coated glass with a sheet resistance of 20 Ω/□ was used as the substrate and anode. All organic layers were successively deposited onto the ITO/glass substrate at a pressure of 1×10^{-4} Pa. The deposition rates for the organic layers and cathode were 0.2 and 0.4 nm s^{-1}, respectively. The emissive area of the device was 5 mm × 5 mm. The EL spectra were measured with Photo Research PR650 Spectra. And the brightness–current density–voltage characteristics of the devices were measured with a Keithley 2400 Source Meter.

Results and discussion

Design and synthesis of host red emitting material

Among the red emitters investigated so far, pyran-containing red dopants, i.e. the DCM analogs are the most promising ones for OLEDs applications. However, they show severe concentration quenching. Chen et al.[2,5] have demonstrated that the reason for concentration quenching is the interaction of dyes in the solid state. Although many efforts have been made to suppress their concentration quenching by introducing bulky groups into the molecule, dopants such as DCJT,[2] DCJTB,[3] and DCJTI[3] still show concentration quenching, and cannot be used as a pure red emitting layer in OLEDs.[3]

In the present work, we introduce two (4-dicyanomethylene)-4H-pyran electron-acceptor moieties into the molecule to form two chromophores. The new design strategy is expected to have the following advantages: 1. the introduction of more electron-withdrawing groups (cyano groups) can increase the electron affinity (EA) of the molecule,[12,13] and improve its electron injection and transport properties; 2. if the molecule containing two chromophores has a non-planar structure, the presence of the bulky chromophores will hinder the regular stacking or arrangement of the molecules in their solid state, and as a result, it may have better ability to reduce the intermolecular interaction in the solid state than those dopants containing only one chromophore.

Owing to its ability to form an ammonium radical cation, and its high hole mobility, the triphenylamine group has been widely used as an efficient hole transport layer for OLEDs, and
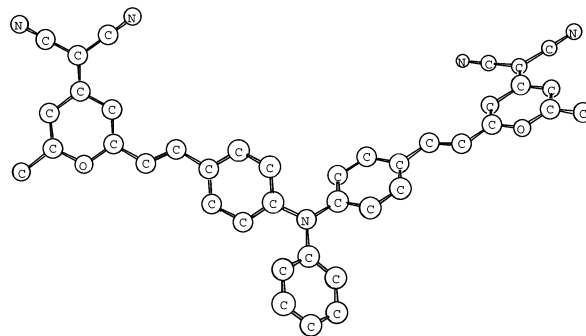

Fig. 1 The minimum energy structure of BDCM.

as an electron donor moiety to modify the EL emitting materials.[17,19] In the present work, we introduce a triphenylamine group into the molecule not only because of its electron-donor properties, but also because of its sterically non-planar structure. As shown in the literature,[20] triphenylamine has a non-planar structure with the N atom deviating from the plane of the bonded C atoms, and there is a dihedral angle of about 75° between any two phenyl rings of the triphenylamine molecule. Based on its non-planar structure, the triphenylamine group ensures that there is a dihedral angle between the two chromophores of BDCM, which can prevent molecules from approaching each other in the solid state, and thus reduce the concentration quenching.

Fig. 1 shows the minimum energy structure of BDCM in the ground state, by using semi-empirical calculations (AM1 method). To make the structure clearer, we show the carbon framework of the molecule only. Although there is a small dihedral angle of 5° between the (4-dicyanomethylene)-4H-pyran moiety and the phenyl ring, the triphenylamine group makes BDCM a twisted structure, which has a large dihedral angle of about 75° between the two DCM chromophores. Compared with dyes containing one chromophore, such as DCJTI, BDCM should have greater ability at preventing the aggregation of molecules in the solid state, and therefore the concentration quenching effect could be greatly reduced.

Absorption and photoluminescence properties

Table 1 lists the absorption and photoluminescence (PL) data of BDCM, DCM-TPA, DCM1, and DCM2 measured in 1,2-dichloroethane (5×10^{-6} M) and in solid films. The corresponding data of DCJT are cited from ref. 2. Compared with DCM2, the absorption and fluorescence maxima of DCM-TPA and BDCM show about 25–45 nm blue shifts both in solutions and solid films. For DCM2 and DCJT, the electron donor moiety of the molecules, the julolidine group is coplanar, and the emission of these dyes shows a much greater red shift compared to that of DCM1. For DCM-TPA and BDCM, the structures of the triphenylamine electron-donor moiety are quite different from that of the coplanar julolidinyl moiety, which makes the emission of DCM-TPA and BDCM blue shift compared with DCM2 in both solutions and solid films.

Table 1 Absorption and PL data in dilute solutions and solid films for BDCM, DCM-TAP, DCM1, DCM2, and DCJT

| Dyes | Absorption λ_{max}/nm | | | Emission λ_{max}/nm | | |
	In solution^a	In solid film	ε^a ($\times 10^4$ M^{-1} cm^{-1})	In solution^a	In solid film	φ_f^c
BDCM	489	505	4.97	583	617	0.87
DCM-TPA	465	474	5.01	588	613	0.93
DCM1	467	478	4.85	576	617	1
DCM2	507	517	5.73	607	645	0.89
DCJT^b	520	—	—	615	—	0.93

^{a}In 1,2-dichloroethane (5×10^{-6} M). ^{b}ref. 2. ^{c}In 1,2-dichloroethane and relative to DCM1.
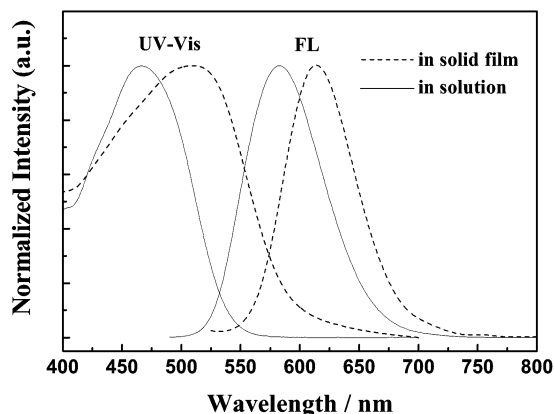
Fig. 2 UV-Vis and FL spectra of BDCM in 1,2-dichloroethane (5 × 10^{-6} M) and in solid film.

The absorption and PL spectra of BDCM in 1,2-dichloroethane (5 × 10^{-6} M) and in solid film are shown in Fig. 2. There was a red shift for both the absorption and emission maxima for BDCM in the solid state compared to those in solution. Such a red shift makes the PL spectrum of BDCM in solid film locate just inside the red region with a peak at 617 nm, suggesting a potential application of BDCM in OLED red emitting materials.

Clearly, the strong red fluorescence of BDCM obtained in solid films was due to the greatly diminished concentration quenching effect, which in turn was the result of the non-planar structure of BDCM.

Electroluminescent performance of BDCM

A three-layered device with the structure ITO/CuPc (50 nm)/ DPPhP (50 nm)/BDCM (50 nm)/Mg:Ag was fabricated and examined. In this device, CuPc was used as a hole injection layer,[17,21] and BDCM as an emitting layer as well as an electron injection and transport layer. For its excellent hole transport ability, pyrazoline has been used as a hole transport material in
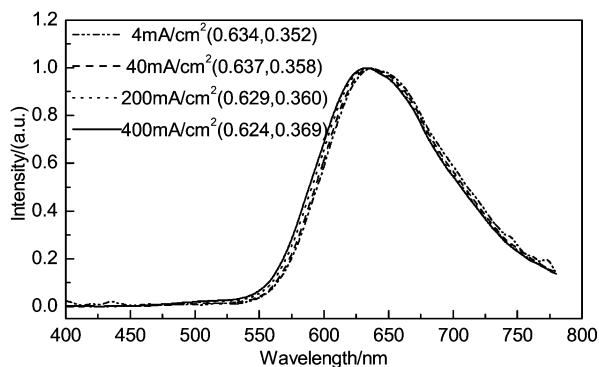

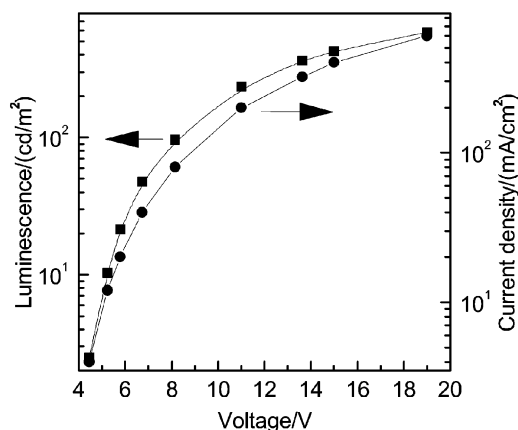**Fig. 3** EL spectra of BDCM at different current densities.

Fig. 4 *I–V–L* curve for the ITO/CuPc/DPPhP/BDCM/Mg:Ag device.

OLEDs.[22] In this research, we used a new pyrazoline with a high melting point, DPPhP, as a hole transport layer.

As anticipated, the EL device using the pure BDCM film as the emitting layer shows a pure red emission with a peak at 640 nm. The EL spectra of the device are presented in Fig. 3. As the films formed by vacuum deposition are more condensed than those fabricated by casting dye solutions, the EL spectrum of the device was found to be red shifted compared with the PL spectrum of a single layer. From the spectra shown in Fig. 3, it can be concluded that the EL emission from the ITO/CuPc/ DPPhP/BDCM/Mg:Ag device comes from the BDCM layer. It can also be seen from Fig. 3 that the emission peak of the device located at around 640 nm, and the CIE coordinates of the device are nearly unchanged with increasing current density. This characteristic offers better device operation compared to red OLEDs with dopants for which the color changes with increasing driving voltage.[10]

The *I–V–L* curve, as shown in Fig. 4, characterizes the properties among the current (*I*), bias voltage (*V*), and the electroluminescence output (*L*). This device emits 2.49 cd m^{-2} at 4.45 V with a current density of 4 mA cm^{-2}, from which a turn on voltage of less than 4 V can be estimated. Since this device has excellent hole injection and transport layers, the low turn on voltage of this device suggests that BDCM must have great electron injection ability.

Table 2 lists the EL characteristics of the present device as well as those published in the literature for a number of reported OLEDs that show red emission, and the molecular structures of DCJT, RED2, PTPQ, and DCDDC are given in Chart 2. Although the breakdown voltage of the device is not examined, the device shows a bright red color emission with a luminescence of 582 cd m^{-2} at 19 V and a current density of 600 mA cm^{-2}. While the doping concentration is below 10%, the color of the device using DCM1 as a guest emitting material turns red. But the maximum brightness of the device is only 150 cd m^{-2} at a doping concentration of 10%, and the pure DCM1 film is almost nonfluorescent. The same case occurs in RED2. Although the maximum brightness of 1400 cd m^{-2} is

Table 2 EL characteristics of red OLEDs

Material/method	L_{max}/cd m^{-2}	$I, V (L_{max})$ (mA cm^{-2}, V)	η_{max}/lm w^{-1}	CIE (x, y) or λ_{max}^{em} (nm)	Ref.
BDCM[a]	582	600, 19	0.059	0.63, 0.36	This work
DCM1[a]	Nonfluorescence	—	—	—	1
DCM1(10)[b]	150	—, 10	—	0.62, 0.36	7
DCM2(10)[b]	1400	2200, 19	0.011	0.64, 0.36	7
RED2(1)[b]	250	130,25	0.042	0.66, 0.33	4
PTPQ[a]	10	500,12	—	622	23
DCDDC[a]	30	—	—	645	6

[a]In solid films. [b]Dopant in host Alq$_3$, the number in the brackets means the dopant concentration.
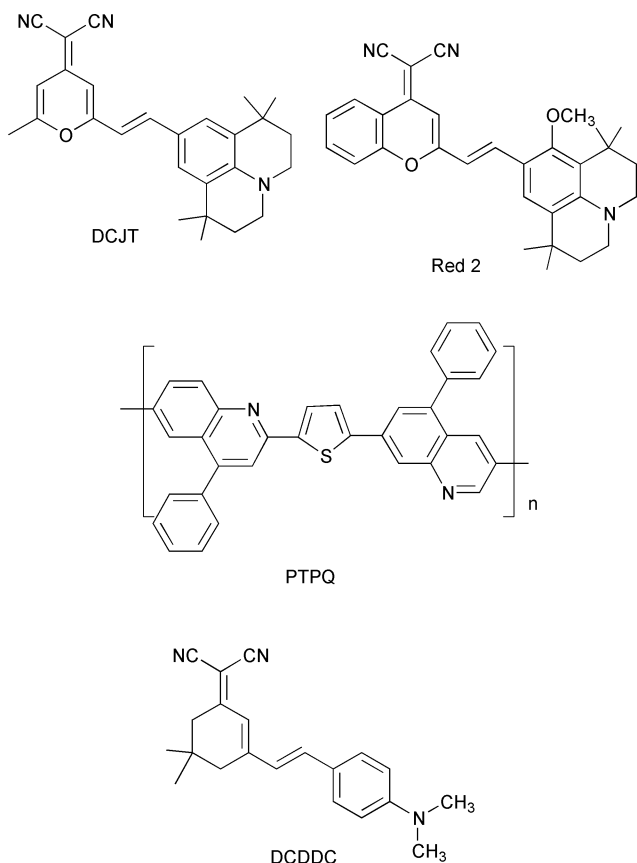
Chart 2 Molecular structures of DCJT, RED2, PTPQ, and DCDDC.

obtained when the doping concentration of DCM2 is about 10%, the lumina efficiency of this device is greatly reduced to 0.011 lm w^{-1}. Compared with the other two red host emitting materials, PTPQ and DCDDC, BDCM shows a brighter red emission. Anyway, the present dye does show an excellent ability to reduce the concentration quenching effect. Based on this work, the further study of BDCM as a dopant and the synthesis of more efficient red dopant materials is in progress.

Summary

A new red-emission dye containing a triphenylamine electron-donor moiety and two (4-dicyanomethylene)-4H-pyran electron-acceptor moieties was designed and synthesized, which has a sterically non-planar structure and good electron injection properties, and can be used as a red host emitter instead of as a dopant. A device with the structure ITO/CuPc(50 nm)/DPPhP(50 nm)/BDCM(50 nm)/Mg:Ag shows bright red emission. The present research presents useful new guidelines for overcoming concentration quenching to obtain more efficient emitters in OLEDs.

Acknowledgement

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