# 6-*N,N*-Diphenylaminobenzofuran-Derived Pyran Containing Fluorescent Dyes: A New Class of High-Brightness Red-Light-Emitting Dopants for OLED

Man-kit Leung,[†,‡] Chin-Chuan Chang,*,[†] Meng-Hsiu Wu,[§] Kai-Hsiang Chuang,[§] Jiun-Haw Lee,[§] Shwu-Ju Shieh,[||] Shien-Chang Lin,[||] and Chi-Feng Chiu[||]

Department of Chemistry, Institute of Polymer Science and Engineering, and Graduate Institute of Electrooptical Engineering and Department of Electrical Engineering, National Taiwan University, Taipei 106, Taiwan, and RiTdisplay Corporation, Hsin Chu Industrial Park 30316, Taiwan

mkleung@ntu.edu.tw

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ABSTRACT

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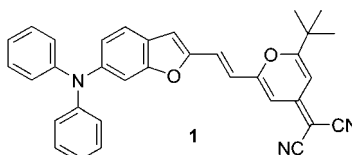
A novel hole-transport moiety for
pyran containing dyes

Dye-doped organic light-emitting diode of ITO/α-NPB (70 nm)/Bebq$_2$-1 (7 nm)/BCP (5 nm)/Bebq$_2$ (33 nm)/LiF (1 nm)/Al (150 nm) shows red electroluminescence with the efficiency of 2.9 cd/A at 100 cd/m^2 and maximum brightness of 62000 cd/m^2. The physical organic aspects of the current-induced fluorescent quenching effect are discussed.

Since Tang and VanSlyke[1] reported a highly efficient organic light-emitting diode (OLED) with high brightness output in 1987, extensive research has been undertaken.[2] Red light is one of the three necessary elements for a full-color display. Although there has been great progress on the development of novel red fluorescent[3] and phosphorescent[4] materials, the family of pyran-containing fluorescent (PCF) dyes is still an important class of red dopants for OLED.[5]

In a typical dye-doped OLED of ITO/α-NPB/Alq$_3$-dopant/ LiF/Al,[6] the PCF dyes are usually doped into Alq$_3$. Energy transfer from excited Alq$_3$ to the PCF dopant leads to red electroluminescence (EL). To avoid the self-quenching effect, the dopant concentration is usually limited at low levels, around 2%. In some cases, the energy transfer process is incomplete, leading the OLED to red-orange emission. To improve the performance of the OLED, Tang and co-workers modified the pyran core to form DCJTB.[7] The presence of the alkyl substituents on DCJTB prevents it from molecular

[†] Department of Chemistry, National Taiwan University.
[‡] Institute of Polymer Science and Engineering, National Taiwan University.
[§] Graduate Institute of Electrooptical Engineering and Department of Electrical Engineering, National Taiwan University.
[||] RiTdisplay Corporation.
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aggregation in the solid state and the self-quenching problem is therefore reduced. However, another problem of current-induced fluorescent quenching (CIFQ) effect was observed.[8] The EL quantum efficiency (QE) of the OLED significantly drops when the applied current-density increases. The loss of QE is attributed to the formation of DCJTB$^+$ that quenches the emission from the excited DCJTB.[9] Therefore, we decide to develop novel red PCF dyes to solve the problem.
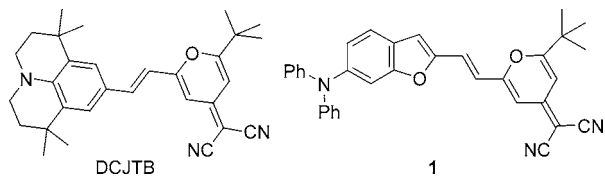
The CIFQ effect of the cationic intermediates is governed by at least two factors: (1) the absorption spectrum and (2) the steady-state concentration of the cationic intermediates in the matrix. The PCF dopants are bipolar compounds that contain an dialkylaminoaryl group linked to an (pyran-4-ylidene)malononitrile component through an olefinic bridge. In our design, a 6-*N,N*-(diphenylamino)benzofuran unit is coupled with a (2-*tert*-butyl-6-vinylpyran-4-ylidene)malono-nitrile unit to give **1**. Triarylamines and furans are good hole-transport materials.[10] We wonder if replacement of the aliphatic amino group by the diphenylaminobenzofuran unit would lead to any positive response on the CIFQ effect and improve the device performance.

The synthesis of **1** was summarized in Scheme 1. *N*-Phenylation of *m*-anisidine was performed under Ullman conditions,[11] followed by BBr$_3$ demethylation to give **2**.[12] Hydroformylation under Vilsmeier conditions led to **3**. Conversion of **3** to benzofuran **4** was performed using the Yoo procedure through intermediate **5**, followed by LAH reduction to give **6**.[13] However, oxidation of **6** to **7** is unexpectedly difficult. Both Swern oxidation or simple PCC oxidation were unsuccessful, leading to **7** in very low yield,
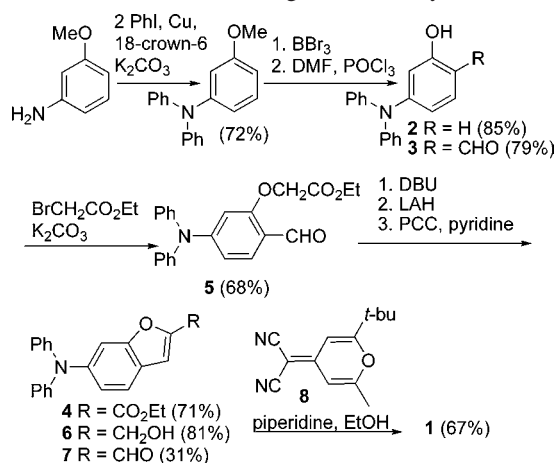
accompanied by several unidentified products. Fortunately, the PCC oxidation in pyridine proceeded to give **7** in 31% yield. Condensation of **7** with **8** gave the desired **1**.

Compound **1** shows a reversible oxidation wave at $E_{1/2} = 0.51$ V against ferrocene standard in the cyclic voltammetry (CV) (Figure 1). The $E_{1/2}$ is about 0.25 V higher than that
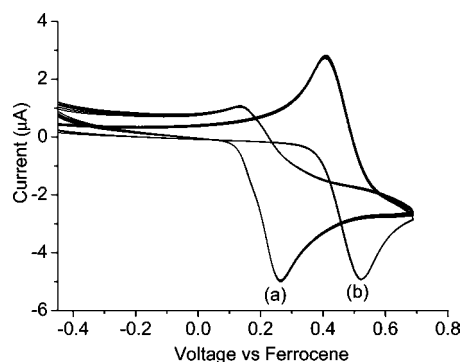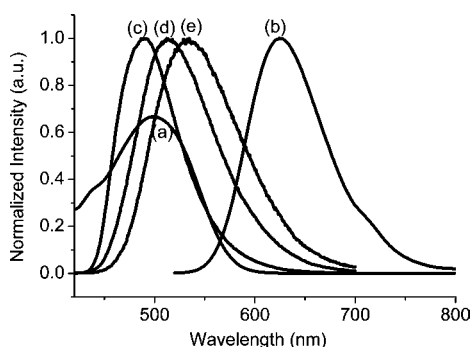

Figure 1. CV plots of (a) DCJTB and (b) **1** in CH$_2$Cl$_2$ with Bu$_4$-NClO$_4$ (0.1 M) as supporting electrolyte. Scan rate: 100 mV/s.

of DCJTB, indicating that **1** has a lower lying estimated HOMO of −5.31 eV.[14] More important is the fact that electrochemical dimerization or polymerization was not observed in the CV experiments. This result suggests that the radical cation **1**$^+$ is electrochemically more stable in comparison to other triarylamine compounds.[15]

Figure 2 shows overlay plots of the UV−vis absorption and emission spectra of **1**, and the emission spectra of common host materials of Bebq$_2$, Alq$_3$, and Gaq$_3$.[16] Compound **1** shows an absorption band peaked at 500 nm with red emission peaked at 624 nm in CH$_2$Cl$_2$. The fluorescence QE is 0.65. Although the spectral overlap of **1** with all three hosts

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Figure 2. (a) UV−vis absorption and (b) PL spectra of **1**, and PL spectra of (c) Bebq$_2$, (d) Alq$_3$, and (e) Gaq$_3$.

is significantly large, almost perfect spectral match with Bebq$_2$ makes them a good couple in the energy-transfer process.[17]

Red OLEDs with both a conventional multilayer structure and a double heterostructure (DH) have been fabricated. To compare the performance of **1** against previous literature data, we adapted Alq$_3$ as the electron transport (ET) material to study. OLEDs with a multilayer structure of ITO/α-NPB (60 nm)/Alq$_3$-**1** (20 nm)/Alq$_3$ (40 nm)/LiF (1 nm)/Al (150 nm) were fabricated.[6] At low dopant concentration of 0.5% of **1**, the EL spectrum showed broad co-emission ranging from 450 to 700 nm, spanning the emission of Alq$_3$ and **1**. When the doping concentrations were gradually adjusted from 0.5 to 5%, significant shifts of the EL λ_{max} from 580 to 650 nm with the OLED efficiency ranged from 0.095 to 0.065 cd/A at 100 mA/cm^2 were observed (Table 1). The EL contribution

Table 1. EL Performance of ITO/α-NPB (60 nm)/Alq$_3$-**1** (20 nm)/Alq$_3$ (40 nm)/LiF (1 nm)/Al (150 nm)

| **[1]** (%)	EL (nm) (λ_{max})	CIE	cd (A)	brightness[a] (cd/m^2)	turn-on voltage[b]
0.5	580	0.46, 0.48	0.085	2700	6.5
2	630	0.61, 0.38	0.095	1500	5.0
5	650	0.63, 0.35	0.065	1700	4.5

[a] At 100 mA/cm^2. [b] V at 100 cd/m^2.

from Alq$_3$ gradually decreased. When the doping concentration was increased to 5%, the CIE coordinates of the EL shifted to (0.63, 0.35). The overall EL efficiency is lower than that of DCJTB. We attribute this to poor energy transfer from Alq$_3$ to **1** due to their poorer spectral match. When the dopant concentration of **1** increased, the device turn-on voltage dropped significantly. This observation suggests that the presence of **1** facilitates hole injection into the emission

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layer. Noteworthy to mention that the CIFQ effect is minimal in this device (Figure 3a). The device efficiency remains almost constant with increasing current density.
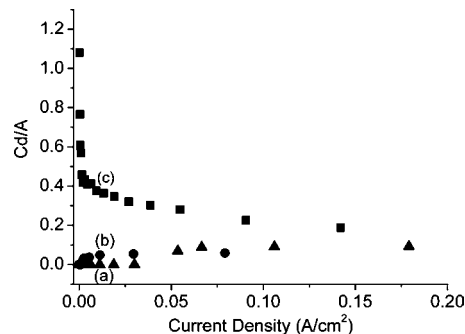
Figure 3. Plots of the EL efficiency vs current density, with various thicknesses of BCP: (a) 0 nm (▲), (b) 2 nm (●), and (c) 20 nm (■).

To elucidate the CIFQ mechanisms, we subjected **1** to a DH OLED of ITO/α-NPB (60 nm)/Alq$_3$-**1** (20 nm)/BCP (20 nm)/Alq$_3$ (20 nm)/LiF (1 nm)/Al (150 nm).[18] In the device, a hole-blocking layer of BCP (20 nm) was introduced to confine the excitions within the recombination zone.[18] The efficiency of the OLED dramatically increased (Table 2) due

Table 2. EL Performance of ITO/α-NPB (60 nm)/Alq$_3$-**1** (20 nm)/BCP (20 nm)/Alq$_3$ (20 nm)/LiF (1 nm)/Al (150 nm)

| **[1]** (%)	EL (nm) (λ_{max})	CIE	cd (A)	brightness[a] (cd/m^2)	turn-on voltage[b]
0.5	600	0.52, 0.45	0.55	3000	8.5
2	648	0.64, 0.35	0.20	1000	9.0
5			0.03	500	11.0

[a] At 100 mA/cm^2. [b] V at 100 cd/m^2.

to higher possibility of charge recombination and exciton formation.

On the other hand, perhaps the presence of the hole-blocking layer enhances the steady-state concentration of **1**$^+$ in the emission zone, the CIFQ effect is significant in these cases (Figure 3c). We managed to record the absorption spectrum of **1**$^+$ (Figure 4) by spectral electrochemistry.[19] The spectral overlap of **1**$^+$ with the emission spectrum of **1**, shown as the shadow area, suggests that **1**$^+$ could be an effective quencher for the S$_1$ state of **1**.

When the thickness of the BCP layer was reduced from 20 to 2 nm, the BCP layer was no longer thick enough to completely block-up the hole migration process. Two distinct emission bands were observed from the EL emission. The

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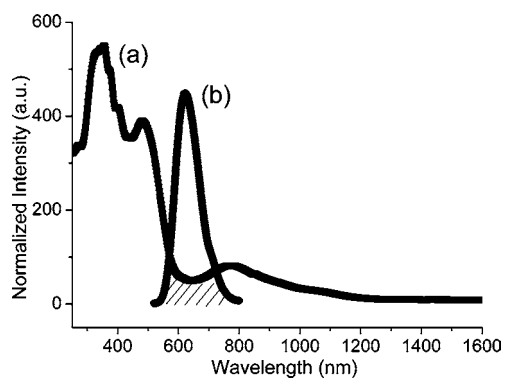
Figure 4. (a) UV−vis−NIR absorption spectrum of $\mathbf{1}^+$ and (b) PL spectrum of $\mathbf{1}$.

band peaked at 510 nm is attributed to the emission of Alq_3 in the ET layer while the other band at 635 nm is assigned to the EL of $\mathbf{1}$ in the emission zone. These results suggest that the holes could partly escape from the emission zone, penetrating the thin BCP barrier, and entering into the Alq_3 zone for recombination. The steady-state concentration of $\mathbf{1}^+$ in the emission zone would therefore maintain at relatively lower level and the CIFQ phenomenon is again minimal (Figure 3b).

The thickness of the emission zone is also an important factor for the EL efficiency. In our study, devices of ITO/α-NPB (70 nm)/Alq_3-$\mathbf{1}$ (0.2%, x nm)/BCP (5 nm)/Alq_3 ($40 - x$ nm)/ LiF (1 nm)/Al (150 nm) with three thicknesses of $x = 7$, 10, and 15 nm for the emission layer were fabricated. Their EL efficiencies were recorded as 1.1, 0.75, and 0.6 cd/A at 100 mA/cm^2, respectively. The EL efficiency increased when the thickness of the emission layer decreased, indicating that the emission zone is confined in a very narrow region, around only 7 nm. This value is in good agreement with the previous conclusion of optimal thickness of 7 nm for DCM study.[18]

The spectral properties of the host materials are important factors for the energy transfer process (Table 3). When Gaq_3

Table 3. EL Performance of the OLED with Different Host/ETL Compounds in ITO/α-NPB (70 nm)/Host-1 (0.5%, 7 nm)/BCP (5 nm)/ETL (33 nm)/LiF (1 nm)/Al (150 nm)

host/ETL	efficiency[a]	maximum brightness[b]
Gaq_3	0.75	12500
Alq_3	1.0	15000
$Bebq_2$	1.8	27500

[a] cd/A at 100 cd/m^2. [b] cd/m^2.

was used, the EL efficiency dropped presumably due to the poor spectral overlap. When $Bebq_2$ was adopted, the maximum EL efficiency was boosted up to 1.8 cd/A with the maximum brightness of 27500 cd/m^2. The efficiency and the CIE coordinates maintained with increasing current density. The higher efficiency of the OLED may be attributed to the effective energy transfer from the excitions in $Bebq_2$ to $\mathbf{1}$.

The EL spectral properties of the $Bebq_2$-based OLED varies when the dopant concentration increases (Figure 5).
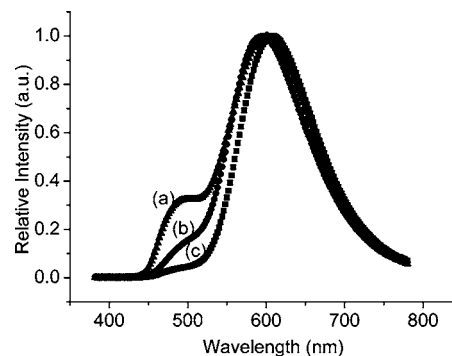
Figure 5. Dopant concentration dependent EL spectra: (a) 0.5%, (b) 1%, (c) 2% of 1 in Bebq2.

When [$\mathbf{1}$] was set at 0.5%, a shoulder of green EL emission at around 500 nm was observed, indicating the energy transfer process is incomplete. The proportion of the green emission significantly reduced when the dopant concentration of $\mathbf{1}$ was increased to 1%. The OLED exhibited good efficiency of 2.9 cd/A at 100 cd/m^2 with the highest brightness of 62000 cd/ m^2. When $\mathbf{1}$ was doped at 2%, the green emission from $Bebq_2$ was almost completely suppressed. The EL efficiency of 1.4 cd/A at 100 cd/m^2 was obtained with the highest brightness of 18000 cd/m^2. Linear relationship between the brightness and the applied current density suggests small CIFQ effect on these OLEDs. The operating lifetimes are longer in comparison to other $Bebq_2$ devices in the literature.[20]

The small CIFQ effect could be attributed to the following factors: (a) The estimated HOMO of $\mathbf{1}$ (-5.31 eV) is only 0.19 eV higher than that of for $Bebq_2$ (-5.5 eV),[16b] indicating that the steady-state concentration of $\mathbf{1}^+$ in $Bebq_2$ should be lower than DCJTB$^+$ (estimated HOMO of DCJTB: -5.11 eV)[14] in Alq_3 (-5.6 eV).[16b] (b) High electron mobility of $Bebq_2$[16b] also leads to effective exciton formation in the emission zone that limit the steady-state concentration of $\mathbf{1}^+$ at low levels.

In summary, $\mathbf{1}$ represents a novel class of red EL dopants. Due to the large Stokes shift of $\mathbf{1}$, $Bebq_2$ can be used as an effective host for $\mathbf{1}$ in the EL device, which is uncommon for other PCF dopants.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of $\mathbf{1-7}$ and their preparation procedures and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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