# A Novel Yellow Fluorescent Dopant for High-Performance Organic Electroluminescent Devices

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We have synthesized a novel yellow dopant (DCTP) for applications in organic light-emitting devices (OLEDs), by introducing a triphenylamine segment as a $\pi$ electron donor and 4-(dicyanomethylene)-2-(*tert*-butyl)-4H-pyran moiety as a $\pi$ electron acceptor to the molecular structure. The resultant dopant has a high fluorescent yield and a sterically well-hindered structure. Its photoluminescence in solution and electroluminescence have been studied. The DCTP-doped OLED with a structure of indium tin oxide/N,N′-bis(3-methylphenyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (TPD)/tris(8-quinolinolato)aluminum ($Alq_3$):2 wt % DCTP/$Alq_3$/Mg:Ag shows a bright yellow emission (chromaticity coordinates: $x = 0.47$; $y = 0.51$) and a brightness of 19 383 cd/m$^2$ at a driving voltage of 20 V. The current efficiency of the device reaches 5.3 cd/A at a current density of 20 mA/cm$^2$ and a voltage of 11 V.

## Introduction

Since the first report of multilayer high-efficiency organic light-emitting diodes (OLEDs),[1] much work has been done to further improve the efficiency and stability of the devices. One very successful method for achieving these improvements is by doping a host organic layer with a dye which has a high fluorescence quantum yield.[2,3] Advantages of the doping method include easy color tuning, higher luminance, improved efficiency, and superior stability of the device.

These advantages have prompted intensive effort in searching for various high-performance fluorescent dopants. To date, a number of blue, green, and red dopants have been reported.[4] Relatively little work, however, has been done on yellow emitting dopants, apart from rubrene.[4,8−10] In this paper, we report the design and synthesis of a new yellow dopant with a high fluorescence quantum yield suitable for OLED applications. Its photoluminescence (PL) in solution and electroluminescence (EL) as a dopant in a solid film have been studied.

## Experimental Section

**Materials and Synthesis.** The new yellow dopant, 4-(dicyanomethylene)-2-*tert*-butyl-6-(*p*-diphenylaminostyryl)-4*H*-pyran (DCTP), was synthesized by Knovenagel condensation. This synthesis was completed by a piperidine-catalyzed reaction between 4-(dicyanomethylene)-2-*tert*-butyl-6-methyl-4*H*-pyran (**1**) and 4-formyltriphenylamine (**2**) in above 65% yield. The key intermediates in this synthesis are compounds **1** and **2**, which were synthesized from pinacolon and triphenylamine (TPA), according to refs 4 and 7, respectively. DCTP directly crystallized from the reaction mixture is highly pure (>99% by HPLC). DCTP was characterized spectroscopically.

*DCTP*: mp 324−325 °C; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.40−7.01 (m,15H), 6.63−6.54 (t,3H), 1.37 (s,9H); MS *m/z* 469 ($M^+$).

**Photoluminescence and Energy Level Measurement.** The absorption and fluorescence spectra of DCTP in a $1 \times 10^{-5}$ M chloroform solution were measured. The fluorescence quantum yield of the compound was estimated by comparing it to a Rhodamine B calibration standard with a known fluorescence quantum yield, $\phi_f$, of 0.67. The ionization potential (IP) and electron affinity (EA) of the organic materials were measured by using ultraviolet photoelectron spectroscopy and UV−visible optical absorption spectroscopy. The absorption and fluorescence spectra were recorded using a Perkin-Elmer Lambda 2S UV−vis spectrophotometer and a Perkin-Elmer LS50 fluorescence spectrophotometer, respectively.

**Preparation of EL Devices and Testing.** EL devices fabricated in this work have a configuration of indium tin oxide (ITO)/TPD (80 nm)/tris(8-quinolinolato)aluminum ($Alq_3$):DCTP (2−5%, 60 nm)/$Alq_3$ (30 nm)/Mg:Ag (200 nm). *N*,*N*′-Bis(3-methylphenyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (TPD) was used as the hole-transporting layer. $Alq_3$ doped with DCTP was used as the emissive layer, and the undoped $Alq_3$ was used as the electron-transporting layer. The DCTP-doped $Alq_3$ emission layer was prepared by coevaporating DCTP and $Alq_3$ simultaneously from two sources at calibrated rates to achieve

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(1) Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.

(2) Shi, J.; Tang, C. W. *Appl. Phys. Lett.* **1997**, *70*, 1665.

(3) Hamada, Y.; Sano, T.; Shibata, K.; Kuroki, K. *Jpn. J. Appl. Phys.* **1995**, *34*, L824.

(4) Chen, C. H.; Shi, J.; Tang, C. W. *Macromol. Symp.* **1997**, *125*, 1.

(5) Chen, C. H.; Tang, C. W.; Shi, J.; Klubek, P. *Macromol. Symp.* **1997**, *125*, 49.

(6) Hamada, Y.; Kanno, H.; Tsujioka, T.; Takahashi, H.; Usuki, T. *Appl. Phys. Lett.* **1999**, *75*, 1682.

(7) Li, X.; Liu, Y.; Liu, M. S.; Jen, A. K.-Y. *Chem. Mater.* **1999**, *11*, 1568.

(8) Sakamoto, G.; Adachi, C.; Koyama, T.; Taniguchi, Y.; Merritt, C. D.; Murata, H.; Kafafi, Z. H. *Appl. Phys. Lett.* **1999**, *75*, 766.

(9) Uchida, M.; Adachi, C.; Koyama, T.; Taniguchi, Y. *J. Appl. Phys.* **1999**, *86*, 1680.

(10) Hamada, Y.; Kanno, H.; Sano, T.; Fujii, H.; Nishio, Y.; Takahashi, H.; Usuki, T.; Shibata, K. *Appl. Phys. Lett.* **1998**, *72*, 1939.

10.1021/cm0004679 CCC: $20.00

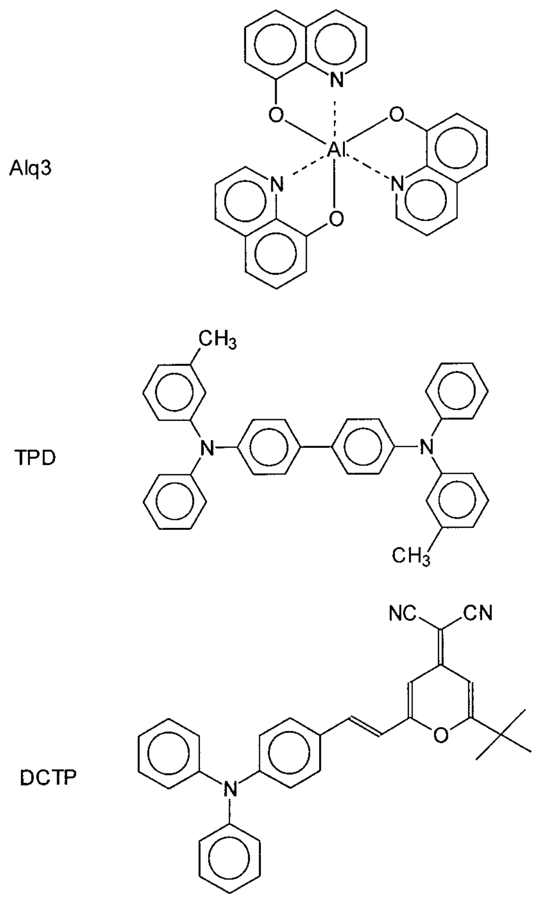

**Figure 1.** Chemical structures of the compounds used in the preparation of EL devices.

the desired mass ratio. ITO-coated glass with a sheet resistance of 50 Ω/square was used as the substrate and anode. All organic layers were successively deposited onto the ITO/glass substrate at a pressure of 5 × $10^{-5}$ mbar. The Mg:Ag (10:1 by mass) cathode was deposited on top of the $Alq_3$ layer at 1.5 × $10^{-6}$ mbar. The deposition rates for the organic layers and the cathode were 0.2 and 0.5 nm/s, respectively. The emissive area of the device was 3 mm × 3 mm. The EL spectrum and brightness–current density–voltage characteristics of the devices were measured with a PR650 Spectra Scan in air at room temperature.

## Results and Discussions

**Molecule Design and Synthesis.** The chemical structures of the compounds used in the EL devices, including that of the new yellow dopant, are shown in Figure 1. It can be seen from its structure that DCTP is a typically intramolecule charge-transfer compound. It consists of an electron donor segment—the triphenylamine moiety—and an electron acceptor segment—the 4-(dicyanomethylene)-2-(*tert*-butyl)-4*H*-pyran moiety. In the design of an intramolecule charge-transfer fluorescent molecule, the following factors have to be considered:[4] (1) the conjugation system; (2) the strength of the electron donor and electron acceptor; (3) the rigidity of the molecule; (4) the steric hindrance.

Typically, red dopants such as DCM2 and DCJTB,[5] which possess a high fluorescence quantum yield, are intramolecule charge-transfer compounds with both strong electron donor and electron acceptor groups. The emission wavelengths of these compounds can be tuned by changing the relative electron donating and accepting abilities of the donor and acceptor groups. To obtain yellow emission with a high fluorescence quantum yield, our approach was to maintain the conjugation system of DCM2 and DCJTB and their molecular rigidity but replace their electron donating group with one that has a lower electron donating ability. Thus, the julolidyl group in DCM2 and DCJTB was replaced by a triphenylamine group, to induce a blue shift in the emission spectrum. In addition, the triphenylamine group has three non-coplanar benzyl groups, which are beneficial for increasing the steric hindrance of the molecule. Furthermore, the introduction of a *tert*-butyl “spacer” group to the DCTP structure is expected to further reduce molecular aggregation and thus the effect of concentration quenching.

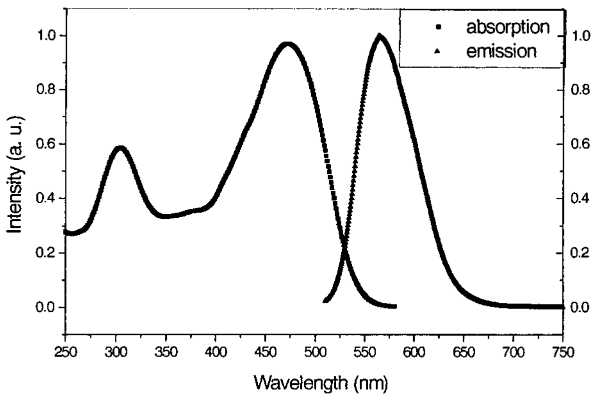

**Figure 2.** Absorption and emission spectra of DCTP in a 1 × $10^{-5}$ M chloroform solution.

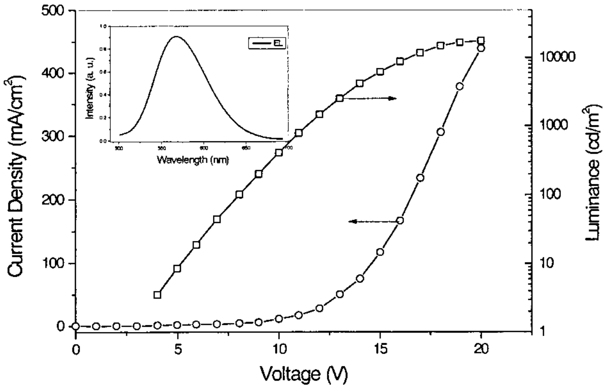

**Figure 3.** Current density–voltage–luminance characteristics of the 2% DCTP doped device. The inset shows the EL emission spectrum.

**Table 1. Photoluminescence Data in Dilute Solution and Energy Levels of the New Dopant**

| dopant | abs $\lambda_{max}$ (nm) | emission $\lambda_{max}$ (nm) | quantum yield (%) | IP[a] (eV) | EA[b] (eV) |
|---|---|---|---|---|---|
| DCPT | 468 | 564 | 94 | 5.6 | 3.4 |

[a] Ionization potential. [b] Electron affinity.

**PL Characteristics and Energy Levels.** The PL absorption and emission spectra of DCTP are shown in Figure 2. The PL peak positions, fluorescence quantum yield, and energy levels of DCTP are summarized in Table 1. These results clearly demonstrate that DCTP is a yellow-emitting compound with high fluorescence quantum yield (94%). The compound also shows a large Stoke shift, and thus the absorption and emission spectra show little overlap. This suggests that the

**Table 2. EL Characteristics of Yellow OLEDs, Including the Reported Maximum Luminance ($L_{max}$) under dc Bias Current ($I$) and Voltage ($V$) at $L_{max}$, Efficiency ($\eta$), and CIE Coordinates**

| material/method | $L_{max}$ (cd/m$^2$) | $I$, $V$ ($L_{max}$) (mA/cm$^2$, V) | $\eta$ (cd/A, lm/w) | CIE ($x$, $y$) | ref |
|---|---|---|---|---|---|
| DCPT in $Alq_3$ (2 wt %) | 19 383 | 440, 20 | 5.3,[a] 1.6[a] | 0.47, 0.51 | this work |
| rubrene in TPDS (5 mol %) | | | 1.87[b] | | 8 |
| rubrene in o-TPD:m-OXD (0.4 wt %) | | | 2.3[c] | | 9 |
| rubrene in NPB (5 wt %) | 27 700 | | 4.2[d] | | 10 |
| rubrene in $Alq_3$ (10 mol %) | 4 200 | | 1.58[d] | | 11 |

[a] At current density $J = 20$ mA/cm$^2$. [b] At current density $J = 10$ mA/cm$^2$. [c] At current density $J = 100$ mA/cm$^2$. [d] Maximum efficiency.

compound should have little self-absorption, which is consistent with the high fluorescence quantum yield of this compound.

Since the IP and EA of DCTP are 5.61 and 3.34 eV, respectively (the corresponding values of $Alq_3$ are 5.62 and 2.85 eV, respectively.),[6] the IP and EA levels of DCTP are located inside those of $Alq_3$. Therefore, electrons and holes are expected to be favorably trapped by the DCTP molecules, so that $Alq_3$ can be used as the host material of DCTP in OLEDs.

**EL Performance.** As mentioned above, the DCTP molecule has a sterically well-hindered structure, which leads to less aggregation and concentration quenching that may suppress, broaden, and red shift the emission. It has be shown by Mi et al. that when molecular aggregation is reduced by adding steric hindrance groups to a molecules, the emission efficiency and spectrum will be relatively insensitive to the concentration of the emitting molecule.[12] For the same reason, we observed no significant difference in the EL spectra and efficiency of the devices with the doping concentration ranging from 2 to 5 wt %. Figure 3 shows the current density−voltage−luminance characteristics of the 2% DCTP-doped device, and the inset shows its EL spectrum. The color is yellow with the emission peak at 567 nm (the CIE color coordinates are (0.47, 0.51)), which is almost identical to the PL peak position of DCTP (reference: PL peaks of DCTP (564 nm), $Alq_3$ (524 nm), and TPD (408 nm)). This indicates that the EL indeed originates only from the DCTP dopant. The device has a turn-on voltage (defined as the voltage required to give a brightness of 1 cd/m$^2$) of 3.5 V and a maximum brightness of 19 383 cd/m$^2$ at 20 V and a current efficiency of 5.3 cd/A at 20 mA/cm$^2$ and 11 V.

Table 2 summarizes the EL characteristics of the present device, as well as those of several recently reported rubrene-doped OLEDs which have a structure similar to that of the present device. It can be seen that the EL performance of the present device is comparable to those of the rubrene-doped devices.

The present work represents an approach to apply the basic photochemistry principles to the design of organic molecules, in order that properties of the resultant molecule can be custom-tuned for specific OLED applications.

## Summary

We introduced a triphenylamine segment as a $\pi$ electron donor and 4-(dicyanomethylene)-2-(*tert*-butyl)-4*H*-pyran moiety as a $\pi$ electron acceptor to a dopant molecule used for OLED applications. This led to the design and synthesis of a novel yellow dopant (DCTP) with a high fluorescence quantum yield and sterically well-hindered structure. The OLED using DCTP as a dopant, and with a structure of indium tin oxide/TPD/$Alq_3$:2wt%DCTP/$Alq_3$/Mg:Ag, shows a bright yellow emission of 19 383 cd/m$^2$ at 20 V. The current efficiency of this device is 5.3 cd/A at 20 mA/cm$^2$ and 11 V. The EL performance of this device is comparable to that of the device with rubrene dopant emitter, a prototypical yellow dopant.

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(11) Huang, J.; Yang, K.; Xie, Z.; Chen, B.; Jiang, H.; Liu, S. *Appl. Phys. Lett.* **1998**, *73*, 3348.

(12) Mi, B. X.; Gao, Z. Q.; Lee, C. S.; Lee, S. T.; Kwong, H. L.; Wong, N. B. *Appl. Phys. Lett.* **1999**, *75*, 4055.