# IMPROVED RED DOPANTS FOR ORGANIC ELECTROLUMINESCENT DEVICES

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Abstract: A *t*-butyl substituted red fluorescent dye, 4-(dicyanomethylene)-2-*t-butyl*-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB), has been found to be an excellent dopant in $AlQ_3$ which produces a highly efficient organic EL device with improved red chromaticity. Unlike 4-(dicyanomethylene)-2-*methyl*-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJT), DCJTB can be synthesized in a pure form directly from the *unsymmetrical* 4-(dicyanomethylene)-2 -(*t*-butyl)-6-methyl-4*H*-pyran without the contamination of the non-fluorescent *bis*-condensation byproduct which is prevalent in the DCJT preparation. Both photoluminescence and electroluminescence in the solid films of DCJTB in $AlQ_3$ are modestly enhanced by the extra t-butyl substitution as a result of a reduction in the effect of concentration quenching. The operation stability of the DCJTB doped EL device is superior, having a half-life of over 5,000 h driven at an initial brightness > 400 cd/m $^2$.

## Introduction

Organic thin-film electroluminescent (EL) devices have received considerable attention due to their potential application in flat-panel displays.[1,2] For color display applications utilizing these organic EL devices, it is necessary to demonstrate a set of primary RGB emitters with a sufficiently high luminous efficiency and proper chromaticity. Such a set of emitters has, in principle, been demonstrated using a guest-host doped system using a single host matrix dispersed with various guest dopants leading to EL emission of many desirable hues.[3] For the red emitter, the red fluorescent laser dyes such as DCM and DCJ were found to be excellent dopants for the $AlQ_3$.[4] However, both the efficiency and the red-shift in EL hue were found to suffer from the well-known effect of "concentration quenching" as a result of interaction among dopants at high concentration. The formation of dopant dimers or higher oligomers which are usually much less fluorescent is presumably responsible for the reduction of luminous efficiency and the concomitant hue shift. It has been shown in our previous work[5] on this class of materials that this concentration quenching effect can be reduced by incorporating a "steric spacer" in the molecular structure to effectively isolate the dopant molecules in the solid $AlQ_3$ matrix. The sterically modified dopant represented by DCJT has produced excellent EL devices with improved red chromiticity.

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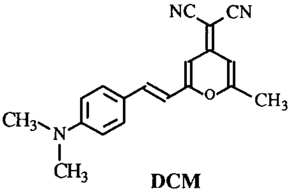
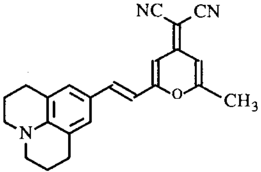


**DCM**

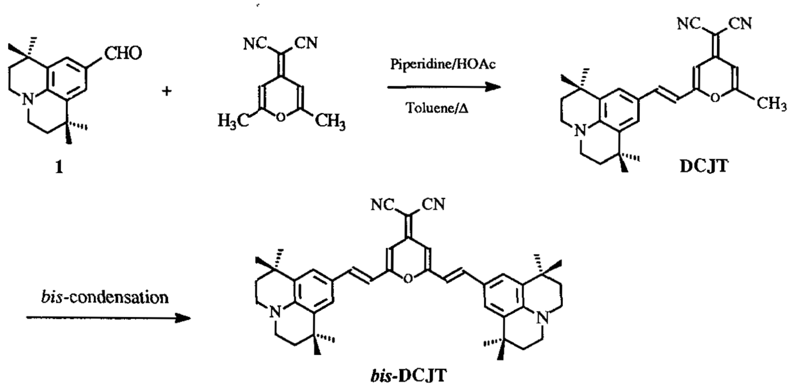


**DCJ**

While the EL performance of *pure* DCJT is satisfactory, the material issue pertaining to its synthesis and subsequent purification remains to be problematical and difficult to control. One of the major drawbacks can be traced directly to the DCJT dye molecule itself which contains an "active methyl" group at the C-6 position of the *pyran* moiety. Under the normal Knovenagel reaction conditions[6] from which these dyes are synthesized, this "methyl" group is still capable of reacting further (albeit at a much slower rate) with the corresponding tetramethyljulolidyl aldehyde (**1**) to form the *bis*-condensed dye designated as "*bis*-**DCJT**", shown in Scheme I. The yield of this byproduct can vary considerably with reaction time, scale and conditions; ranging from 5.5% to as high as 19%. Furthermore, once the byproduct is formed in the DCJT-product mixture, it is very difficult to be removed without subjecting to tedious chromatographic separation and/or fractional sublimation procedures. Similar complication has also been noted in the preparation of DCM whose *bis*-condensed product is identified as the 4-(dicyanomethylene)-2,6-bis(*p*-dimethylaminostyryl)-4*H*-pyran[7] which is found to absorb the DCM fluorescence band, thus significantly diminishing or extinguishing its fluorescence. *bis*-**DCJT** is no exception due to the fact that it has a broad and very weak fluorescence peaking near 675 nm in dichloroethane with a quantum yield of only 8% of that of DCJT. The inadvertent contamination of this byproduct in the red dopant DCJT can have a significant quenching effect on its fluorescence which eventually will manifest itself in the poorer EL performance of a DCJT doped $AlQ_3$ cell.

In this report, we will describe the synthesis of an improved red dopant, DCJTB, which is free (by design) from any possible contamination of the *bis*-condensation byproduct from its reaction. As a result, the uncertainty surrounding the purity issue of the red dopant can be resolved. It will be shown that DCJTB has a slight but significant advantage over DCJT in EL efficiency as well as in chromaticity at high

**Scheme I. Synthesis of DCJT**

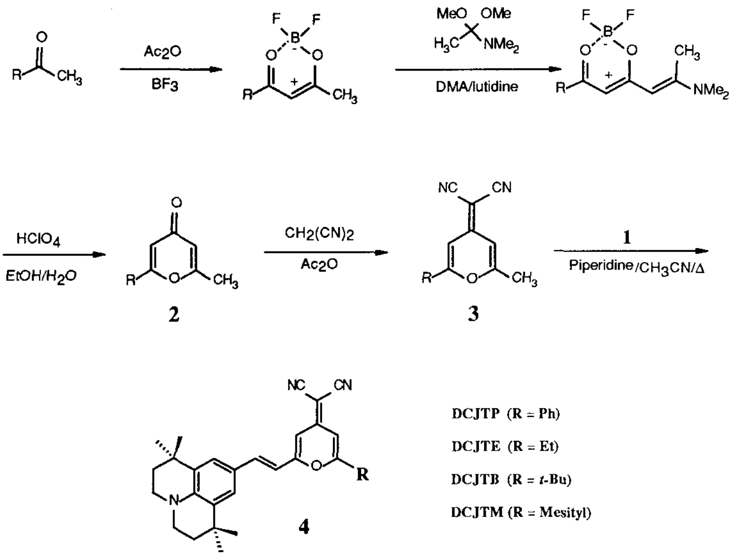


doping concentration in $AlQ_3$. Finally, the long term operational stability of a DCJTB doped EL cell will also be reported.

## Design and Synthesis

From the chemistry point of view, the best way to eliminate the complication of the remaining "active methyl" group on DCJT is to replace it with something that's not reactive. For this requirement, one needs to look for a means of synthesizing the *unsymmetrical* 4-(dicyanomethylene)-2-methyl-4*H*-pyran (**3**) which is usually prepared from the corresponding 4H-pyran-4-one (**2**). Both the phenyl[5] and ethyl[8] substituted compound **2** (R = Ph and Et) are known. Other bulky substituents such as *t*-butyl and mesityl can be synthesized by the new method outlined in Scheme II.[9] The desired red fluorescent dyes **4** can then be prepared by Knovenagel condensation of **3** with the tetramethyljulolidyl aldehyde (**1**) as shown.

**Scheme II. Synthesis of *Unsymmetrical* 4-(Dicyanomethylene)-2-methyl-4H-pyrans and New Dopants**



The yields and purity of the new red dopants **4** synthesized under two different reaction conditions are compared with those of DCJT in Table 1. It is clear from the results that the best yield and purity of products are derived from the *unsymmetrical* pyrans which contain no α-hydrogen at the *pyran* ring, e.g. DCJTB, DCJTP and DCJTM. The *ethyl*-substituted DCJTE (**4**, **R** = Et) which contains two α-hydrogens is apparently still capable of forming a small amount (1.2%) of *bis*-condensed dye contaminant in the reaction.

**Table 1. Comparison of Syntheses of New Dopants 4 and DCJT**

| Dye | Reaction[1] | Yield | Purity[2] | *bis*-Condensed Impurity |
|---|---|---|---|---|
| DCJT | A | 90% | 80% | 19% |
| DCJT | B | 50% | 94% | 5.5% |
| DCJTB | A | 79% | 99.3% | 0% |
| DCJTB | B | 44% | 99.3% | 0% |
| DCJTE | A | 63% | 98.4% | 1.2% |
| DCJTM | B | 64% | 97.6% | 0% |
| DCJTP | B | 75% | 99.9% | 0% |

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1. A: cat. Piperidine/HOAc/Toluene/Reflux. B: cat. Piperidine/$CH_3CN$/Reflux.
2. HPLC analysis at 440 nm.

### Photoluminescence

The fluorescence spectra were recorded on a FluoroMax 2 instrument using 490 nm as the excitation wavelength. Table 2 compares the relative radiance, luminance efficiencies, and emission maxima of the new dopants **4** with those of DCM and DCJT in dilute 1,2-dichloroethane solution. It is concluded from these results that DCJTP (**4**, **R** = Ph) which contains a phenyl ring that can conjugate with the chromophore emits too far to the red (at 654 nm). Due to the free rotation of the phenyl substituent which tends to enhance the probability for nonradiative decay[10], the radiance and luminance efficiencies of DCJTP are too low for this compound to be useful as a red dopant in EL applications. Bulkier substituents such as the mesityl group (2,4,6-trimethylphenyl) in DCJTM can force the phenyl group to twist away from the plane of conjugation, thus restricting the degree of free rotation about the single bond connected to the phenyl ring. As a result, DCJTM recovers most of the radiance efficiency inherent in the chromophore. However, its peak emission at 636 nm, coupled with the large bandwidth (~100 nm) typical of this class of dyes, is too red-shifted to be useful in EL application. The alkyl substituted DCJTE (**4**, **R** = Et), and DCJTB (**4**, **R** =t-Bu) stand out from this group as being the most efficient in the radiance output while the emission spectra are centered not too deep into the red as in the case of the phenyl substituted dyes. The additional *t-butyl* "spacer" group in DCJTB is expected to be advantageous in further reducing the effect of concentration quenching.

**Table 2. Comparison of Fluorescent Properties of Red Dopants**

| Dyes | Radiance[a] | Luminance[a] | λ max[b] (nm) |
|---|---|---|---|
| DCM | 1.0 | 1.0 | 585 |
| DCJT | 1.58 | 0.89 | 618 |
| DCJTB | 1.70 | 1.01 | 615 |
| DCJTE | 1.52 | 0.88 | 622 |
| DCJTM | 1.46 | 0.67 | 636 |
| DCJTP | 0.30 | 0.09 | 654 |

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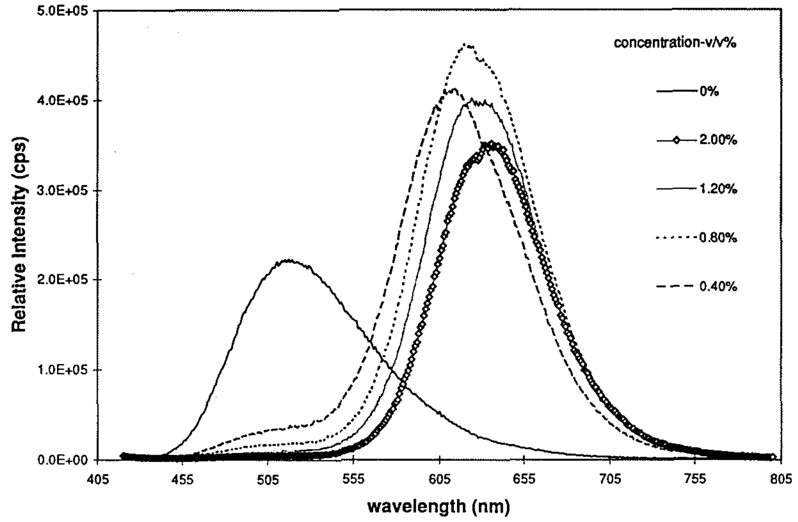
a. Relative to DCM
b. Measured in 1,2-dichloroethane

Fig. 1 shows the effect of doping concentration of DCJTB on the fluorescence spectra of thin film $AlQ_3$ prepared by co-evaporation. By comparison with the previously published data on DCJT[4], it is found that, at high concentration, the effect of concentration quenching of PL emission can be further minimized by introducing the extra *t*-butyl substituent in DCJTB which reduces the interaction between the guest molecules in the $AlQ_3$ matrix.

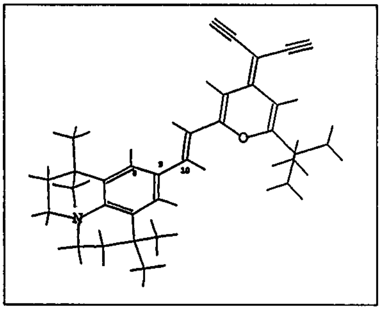
Fig. 1 DCJTB Fluorescence using AlQ$_3$ as Host



## Characterization of DCJTB

Pure DCJTB has a melting point of 294° C. No glass transition temperature was detected by DSC up to its melting. The thermal decomposition temperature is around 305 ° C. FDMS shows a $(M^+ + 1)$ peak at *m/e* 454 for $C_{30}H_{35}N_3O$. Cyclic Voltammogram of DCJTB scanned at 20V/s in methylene chloride (0.1 M TBABF$_4$) using a 25 micron Pt ultramicroelectrode vs SCE produces a $E_{ox}$ +0.76 v and $E_{red}$ -1.37 v. Single crystals of DCJTB can be obtained by slow evaporation of a toluene solution. An X-ray crystallographic picture of DCJTB is reproduced in Fig. 2. As expected, the nitrogen which represents the donor part of the molecule is held coplanar to the phenyl ring of the julolidine. The "dicyanomethylene" which represents the acceptor part of the dye chromophore is also flat in conjugation with the julolidine ring. These two moieties are connected by a "trans" double bond as confirmed by this analysis. There exists a slight twist around C-9 and C-10 single bond with a torsional angle of about 11° which is presumably caused by the steric interaction between $H_8$ and $H_{11}$. The *t-butyl* group at the acceptor side of the chromaphore appears to exert no impact on the integrity of the donor-acceptor chromaphore. As noted before, this makes the *t-butyl* substituted on DCJTB an ideal "spacer" group in reducing the effect of concentration quenching. The tetramethyl groups on the donor part of the dye chromophore assume pseudo equatorial configurations. Including Van der Waals forces, it is estimated to protrude about 2Å above and below the imaginary plane of the donor-acceptor chromophore.

**Fig. 2 A Single Crystal X-ray Crystallographic View of DCJTB**



## Electroluminescence of DCJTB Vs DCJT

The organic EL device was fabricated by vapor deposition according to published procedures.[11] The sequence of deposition and respective layer thickness were: [ITO (300 A)/CuPc (150 A)/NPB (600 A)/$AlQ_3$ (375 A) + red dopant/$AlQ_3$ (375 A)/Mg:Ag (10:1. 2000 A)]. The EL device was completed with encapsulation in a dry argon glove box. The structures of CuPc, NPB, and $AlQ_3$ have been disclosed previously.[4] The EL luminance and chromaticity values were measured using a Photo Research PR-650 spectrophotometer.

The EL efficiency versus doping concentration (v/v % in $AlQ_3$) is shown in Fig. 3, comparing DCJTB with DCJT. At low concentration levels, the EL efficiencies of both dopants increase steadily with concentration peaking at a dopant concentration of 0.4%. But, as the doping concentration increases further, the EL efficiencies for both dopants decreases steadily. This decrease in efficiency appears to be somewhat less in DCJTB than in DCJT, attributing to the extra spacer tetramethyl group in DCJTB. A similar trend was noted in the photoluminescence data as well. The color of the EL devices is compared in Fig. 4 using the CIE color coordinates representation. It can be seen that the color of the DCJTB doped EL is slightly red-shifted relative to that of the DCJT for all concentration levels.

**Fig. 3 El Performance of Red Dopant DCJTB vs. DCJT**

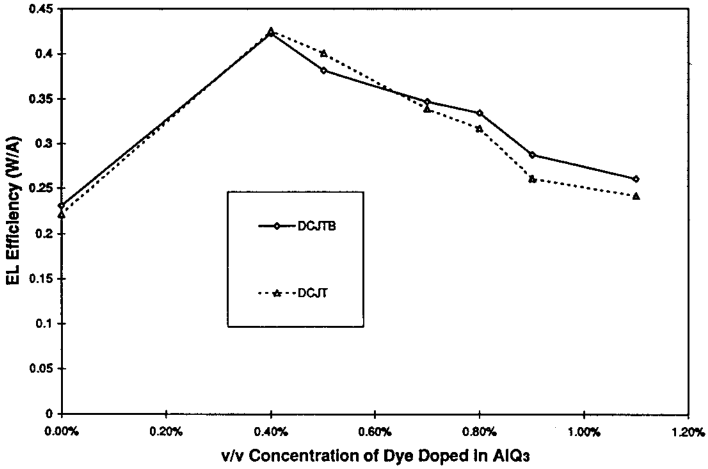


**Fig. 4 El Color of DCJTB vs. DCJT**

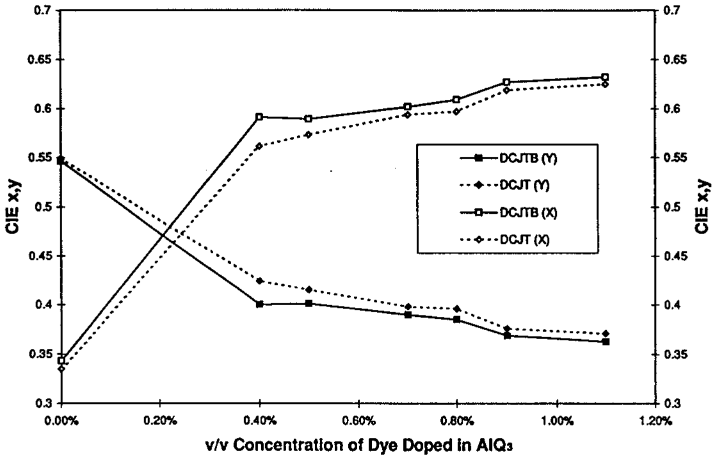
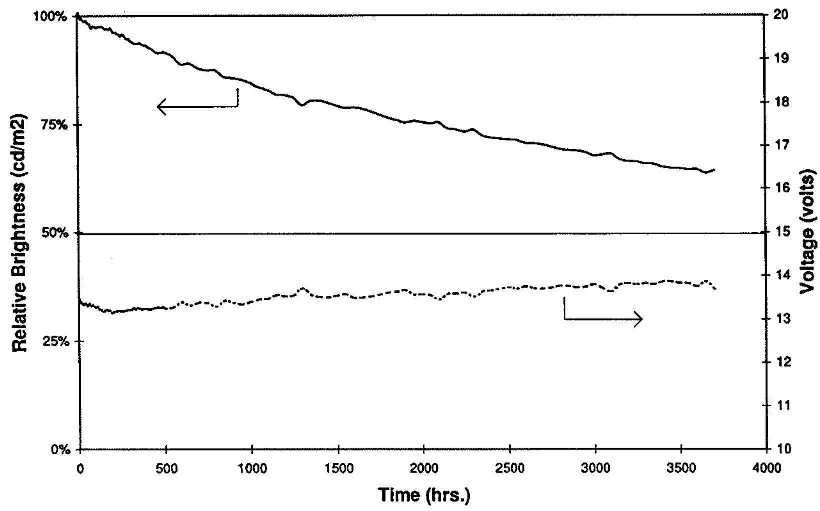


Fig. 5 Operational Stability of DCJTB Doped AlQ3 EL Device



**Operational Stability of DCJTB Doped Device**

For the operational stability test, a constant current source was used with a modified waveform to include a constant reverse voltage component. The test conditions are as follows: 40 mA/cm$^2$ constant current in the forward bias cycle and -14 V in the reverse bias cycle, 1 kHz square wave, and 50% duty cycle. Fig. 5 shows the operational stability of a DCJTB doped device with initial luminance of 439 cd/m$^2$ normalized to 100%. The EL device has a DCJTB concentration of ~0.5% in $AlQ_3$, a peak emission wavelength at 620 nm, and CIEx,y coordinates of 0.617; 0.377.

The aging behavior of the EL device is similar to the undoped Alq device we reported recently.[11] The luminance decay is continuous with operation and the rate of decay becomes progressively slower. Beyond 1,500 hours, this decay rate is about 0.02 cd/m$^2$ per hour. The drive voltage remains relatively constant, rising by approximately 0.5 V after a drop of similar magnitude in the initial hundred hours. The mean time to half-brightness (or half-life) for this red DCJTB doped EL device well exceeds 5,000 h under these test conditions.

## Summary

It is found in this study, DCJTB can be synthesized in pure form directly from the *unsymmetrical* 4-(dicyanomethylene)-2 -(*t-butyl*)-6-methyl-4*H*-pyran (3, R = *t-butyl*) without the contamination of the potentially quenching "*bis*-condensation" byproduct which is prevalent in the DCJT preparation. The incorporation of the extra *t-butyl* group as a "steric spacer" has a slight but very significant advantage on the EL performance of DCJTB doped devices over those of DCJT by eliminating the concentration quenching effect. DCJTB also improves the red chromaticity. The operational stability of the DCJTB doped EL device iswell over 5,000 h driven at an initial brightness > 400 cd/m $^2$.

## Acknowledgement

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