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Efficient Green Coumarin Dopants for Organic Light-Emitting Devices

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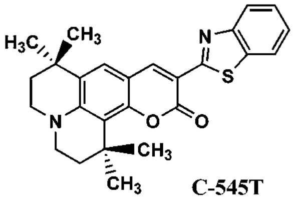
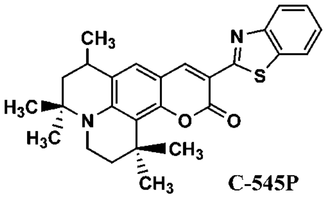
ABSTRACT



C-545T



C-545P

We have synthesized a new green fluorescent dopant C-545P having incorporated five strategically placed "methyl" steric spacers on the julolidyl ring system. C-545P has good thermal properties and photostability, and when fabricated as a dopant in an Alq$_3$-hosted OLED device, it shows notable improvement in luminance efficiency and is more resistant to concentration quenching than C-545T, particularly in the doping concentration range between 1 and 2% v/v, while achieving comparable device stability.

One of the key developments in the advancement of organic light-emitting device (OLED) technology for flat panel display applications can be attributed to the discovery of the guest−host doped emitter system.[1] This is because a single host with optimized transport and luminescent properties such as tris(8-hydroquinolinato)aluminum (Alq$_3$) may be used together with a variety of highly fluorescent or phosphorescent guest dopants leading to electroluminesence of desirable hues with very high efficiencies. Another advantage of the doped emitter system in OLED is the enhancement of its operational stability by transferring the electrogenerated exciton to the highly emissive and stable dopant site thus minimizing its possibility for nonradiative decay.[2] In fluorescent dopants, one of the best green dopants used in many of today's OLED prototypical products is 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*]-pyrano[6,7,8-*ij*]quinolizin-11-one (C-545T).[3] These include, for example, monchrome and area color passive dot-matrix displays first introduced to the market by Pioneer,[4] prototype of passive-matrix full-color OLEDs, in 1998 followed by Kodak/Sanyo's 2.4" QVGA AMOLED exhibited at JES'99[5] and a 5.5 LTPS QVGA active-matrix full-color OLED display shown at SID 2000.[6]

However, upon further examination of the relationship between electroluminescent (EL) efficiency (cd/A) and doping concentration, it is revealed that the luminance efficiency of C-545T tends to drop rather quickly after peaking at around 1%. This narrow window of optimal doping concentration and the lack of robustness in process control for fabrication of the doped emitter can be disadvantageous in production where high display quality assurance is required.

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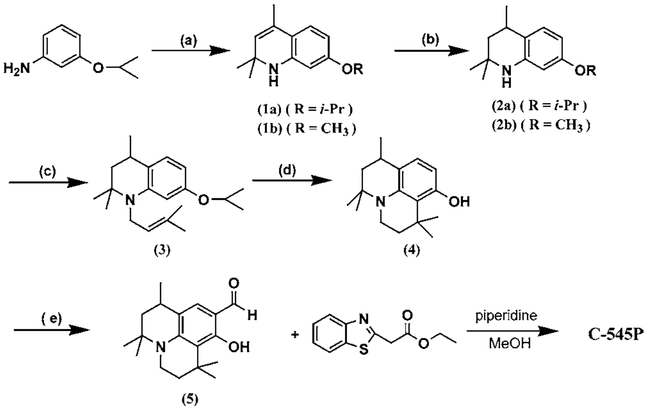
Recently, a sterically bulky di(*tert*-butyl)-substituted derivative, 10-[2-(5,7-di-*tert*-butyl)-benzothiazolyl-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*]-pyrano-[6,7,8-*ij*]quinolizin-11-one (C-545TB) was found to be superior to C-545T in terms of thermal properties, EL performance, and, in particular, its resistance to concentration quenching.[7] However, as reported in the cited patent literature,[8] the synthesis of C-545TB was rather tedious and expensive.

In this letter, we report an alternative derivative, 10-(2-benzothiazolyl)-1,3,3,7,7-pentamethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*]-pyrano[6,7,8-*ij*]-quinolizin-11-one (abbreviated as **C-545P**), which can be successfully synthesized by a simple procedure. Having five strategically placed "methyl" steric spacers, the molecular design feature of **C-545P** is quite different from that of C-545T. Notably, there are now two *gem*-methyl groups substituted α- to the lone pair p-orbital of the nitrogen of the julolidyl ring system in **C-545P**. From the perspective of stereochemistry, the lack of molecular symmetry in the pattern of methyl substitution on julolidyl ring is expected to prevent molecular aggregation and thus could further delay the onset of concentration quenching at a high doping concentration. When fabricated as a doped green emitter in OLEDs, this new green dopant **C-545P** notably improves the EL performance over the corresponding C-545T as well as its thermal properties, photostabiltiy, and device stability without affecting its emissive color.

The synthesis of **C-545P** is outlined in Scheme 1 in which one of the key steps is the acetone-anil reaction[9] for the preparation of 7-(*i*-propyloxy)-2,2,4-trimethyl-1,2-dihydroquinoline (**2a**). This is accomplished from *m*-(*i*-propyloxy)aniline (**1a**) by heating with acetone in the presence of a catalytic amount of iodine at elevated temperature. Selective protection of the hydroxy group in *m*-aminophenol is readily achieved by alkylation of the phenolate that can be generated by "super base" with powder KOH in DMSO at low temperature with *i*-propyl bromide. Although a similar reaction has been reported for *m*-methoxyaniline (**1b**), the cyclization was found to produce a 5-methoxy-substituted isomer (35%) in addition to the desired 7-methoxy-isomer (**2b**) (46%). This lack of regioselectivity is attributed to the electron-donating properties of both alkoxyl and amino groups, which direct the annulation toward both their ortho and para positions.[10] The excess contamination of the 5-isomer in the reaction mixture caused considerable problems in separation (by column chromatography), purification, and scale-up of the reaction.

Scheme 1



To alleviate the regioisomer problem, a bulky *i*-propyl group is substituted in place of the methyl, as in *m*-(*i*-propyloxy)aniline (**1a**) in the present scheme, as the Friedel−Crafts cyclization is known to be controlled more by steric than electronic factors. As expected, the desired 7-(*i*-propyloxy)-2,2,24-trimethyl-1,2-dihydro-quinoline (**2a**) can be produced predominantly over the 5-isomer with a ratio of more than (93:7) as estimated by the ^{1}H NMR integration of their corresponding C-4 methyl singlets at δ 1.84 and 2.18, respectively. The lack of isomeric contamination of the acetone-anil reaction allows the desired 7-(*i*-propyloxy)-substituted isomer to be separated readily by recrystallization in 85% yield without needing column chromatography. Catalytic hydrogenation proceeds smoothly to give the 7-(*i*-propyloxy)-2,2,4-trimethyl-1,2,3,4-tetra-hydroquioline (**3**), which can be alkylated with 1-chloro-3-methyl-2-butene followed by acid-catalyzed cyclization according to a patented procedure[11] to give the key intermediate 8-hydro-1,3,3,7,7-penta-methyl-julolidine (**4**) directly with concomitant loss of the protective *i*-propyloxy group. Vilsmeir formylation of **4** then gives rise to 9-formyl-8-hydroxy-1,3,3,7,7-pentamethyljulolidine (**5**), which is condensed with ethyl (2-benzthiazolyl)acetate[12] under Knoevenagel conditions to give the desired **C-545P** in 83% yield. The molecular structure of **C-545P** was confirmed by ^{1}H and ^{13}C NMR and elemental analysis. Its purity was checked by TLC as well as HPLC (>99%), and its mass spectrum revealed no

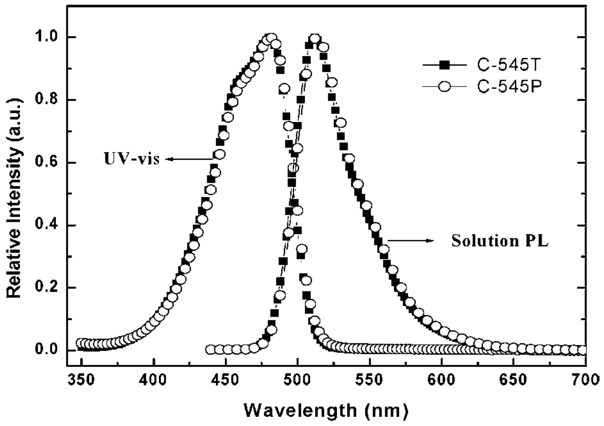


Figure 1. Optical absorption and photoluminescence (PL) spectra of **C-545P** and C-545T.

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extraneous peak other than the desired parent $m/e = 444$ (M^+ for $C_{27}H_{28}N_2O_2S$).

Figure 1 shows the optical absorption and photoluminescent (PL) spectra of a dilute solution of **C-545P** in 1,2-dichloroethane in comparison with those of C-545T, and their spectral data and quantum efficiency are given in Table 1.

Table 1. Spectral, Thermal, and Electrochemical Data of C-545T and **C-545P**

	$\lambda_{max}{}^{abs}$ (nm)	$\lambda_{max}{}^{PL}$ (nm)	Φ_f	T_g (°C)	T_m (°C)	T_d (°C)	E^{ord} (V)
C-545T	480	512	1	100	230	318	0.47
C-545P	480	514	0.99	102	252	343	0.47

Both of their UV−vis absorption and PL spectra are essentially superimposable with the fluorescence λ_{max} of **C-545P** at 514 nm, which is only 2 nm longer than that of C-545T. Their emission bands with full width at half-maximum (fwhm) of 48 nm are also identical, and so are their respective quantum yields, with that of **C-545P** being only 1% less than that of C-545T.

The thermal property of **C-545P** was evaluated by means of thermogravimetric analysis (TGA) in a nitrogen atmosphere. The weight loss of **C-545P** is less than 5% upon heating to 343 °C, which is 25 °C more thermally stable than that of C-545T. The glass transition temperature (T_g) of **C-545P** was determined by differential calorimetry (DSC) to be 102 °C, which is similar to that of C-545T.

By cyclic voltammetric (CV) measurements, samples (C-545T and **C-545P**) were dissolved in deoxygened acetonitrile with tetra-*n*-butylammonium tetrafluoroborate as the electrolyte. A platinum working electrode and a saturated Ag/AgCl reference electrode were used. Ferrocene was used for potential calibration (all reported potentials are referenced to ferrocene/ferrocenium). The HOMO and LUMO levels were calculated by the following equation[13] (HOMO $= E^{oxd}$ (or E^{oxd}_{onset}) $+ 4.8$; LUMO $=$ HOMO $- E_g$) and the band gap energy (E_g) was calculated from the edge of UV−vis absorption peak. The band gap energies of both of these green dopants are estimated to be 2.4 eV with the HOMO at −5.3 eV and the LUMO at −2.9 eV and are most conductive for energy-transfer from the Alq_3 host with the HOMO and the LUMO at −5.5 and −2.7 eV, respectively.

The EL properties of the new dopant **C-545P** are evaluated in the device structure of ITO/CuPc (15 nm)/NPB (60 nm)/v% dopant + Alq_3 (37.5 nm)/Alq_3 (37.5 nm)/LiF (1 nm)/Al (200 nm), where the ITO on glass with a SiO_2 barrier layer was used as the substrate with a sheet resistance of 20 ohm/sq, CuPc (copper phthalocyanine) as the hole-injection layer, NPB (1,4-bis[*N*-(1-naphthyl)-*N*′-phenylamino]biphenyl) as the hole transport layer, dopant $+Alq_3$ as the emitter, Alq_3 as electron transport layer, and LiF as the electron-injection layer. The layer structure of the doped device and the corresponding HOMO−LUMO energy levels are depicted in Figure 2.

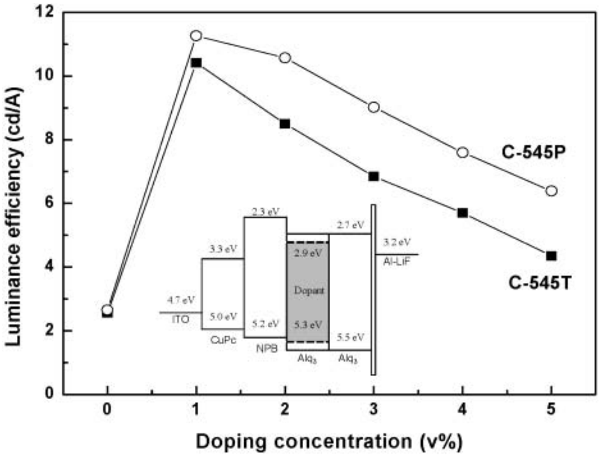

Figure 2. Doping concentration vs luminance efficiency of **C-545P** and C-545T and energy diagram of doped green OLEDs (inset).

All EL devices were fabricated according to a protocol previously established at Kodak.[14] The active area of the EL device, defined by the overlap of the ITO and the cathode electrodes, was 9 mm^2. The EL device was completed with encapsulation in a dry nitrogen glovebox. The EL emission spectra and current−voltage−luminance characteristics of the devices were measured with a diode array rapid scan system using a Photo Research PR650 spectrophotometer and a computer-controlled dc source.

The plots of doping concentration (v/v %) in Alq_3 vs luminance efficiency (cd/A) of **C-545P** and C-545T are compared in Figure 2. Both dopants have their peak efficiencies at around 1% with **C-545P** showing better luminance efficiency of 11.3 cd/A and power efficiency of 4.6 lm/W as compared to those of C-545T of 10.4 cd/A and 3.9 lm/W, respectively. At optimal concentration, the emissive colors of both devices expressed in terms of 1931 CIE coordinates are essentially identical at around (0.31, 0.65). From the profile of the curves, the luminance efficiency of **C-545P** in the doping concentration range of 1−2% has dropped only 6%, but that of C-545T has dropped more than 20%. It is notable that **C-545P** is more resistant to concentration quenching than C-545T, particularly in the doping concentration range between 1 and 2%. In addition, the descending trend of both curves is similar over 2%; the absolute luminance efficiency of **C-545P** is, however, higher than that of C-545T in that doping range.

Figure 3 shows the comparison of both devices doped at the optimal concentration of 1%. Like C-545T, **C-545P**

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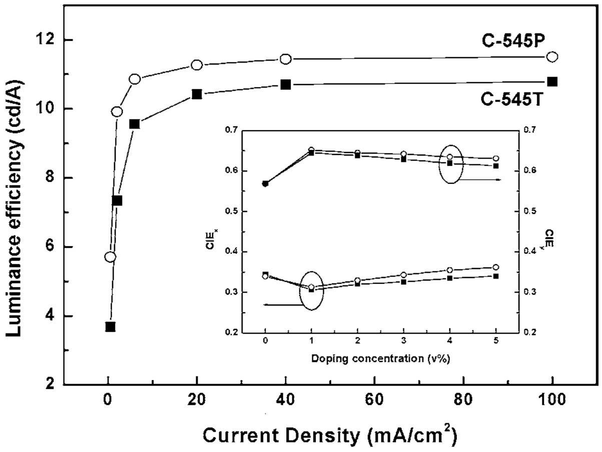

Figure 3. Luminance efficiency vs current density and doping concentration vs 1931 CIE_{xy} coordination (inset) of **C-545P** and C-545T.

displays a nearly flat response of luminance efficiency (cd/A) with respect to a wide range of drive current conditions from 10 mA/cm^2 and an earlier plateau to 100 mA/cm^2 at all doping concentrations. **C-545P** also shows a much steeper rise and reaches the plateau in efficiency earlier than C-545T in the low-drive current region. This is particularly desirable for the passive-matrix displays, where the system would need to be capable of high luminance at low voltage and have a "flat" cd/A respond with respect to drive voltage for the IC drive circuit design. In the insert, the emissive color of both **C-545P** and C-545T expressed in 1931 CIE coordinates are plotted against their respective doping concentration. The robust nature of the green **C-545P** doped emitter in terms of color variation is also comparable with that of C-545T.

Figure 4a shows the photostability of **C-545P** vs C-545T. In a photostability study, samples were irradiated with a 400 W high-pressure mercury lamp (λ = 254~600 nm) in acetonitrile under ambient conditions to study their fluorescent decay with time of radiation. It was found that the half-life ($t_{1/2}$) of **C-545P** was about 5 h, while that of C-545T was much shorter (3 h). The device operational stability test is shown in Figure 4b. L_0, measured at the green device of 1% **C-545P** and C-545T doped in Alq_3, was 2847 and 2779 cd/m^2, respectively. From an extrapolation of the curve to half the initial luminance of **C-545P** and C-545T, $t_{1/2} = 425$ and 425 h, respectively. Assuming the scalable Coulombic degradation,[14] for driving at L_0 of 100 cd/m^2, $t_{1/2}$ of **C-545P** and C-545T are projected to be 12 100 and 11 810 h, respectively.

In conclusion, we have successfully synthesized a new green fluorescent dopant **C-545P** by a simple procedure. The new green dopant **C-545P** has good thermal properties and photostability, and when fabricated as a dopant in an Alq_3-hosted OLED device, it shows notable improvement in luminance efficiency and more resistance to concentration quenching than C-545T, particularly in the doping concentration range between 1 and 2% v/v, while achieving comparable device stability.

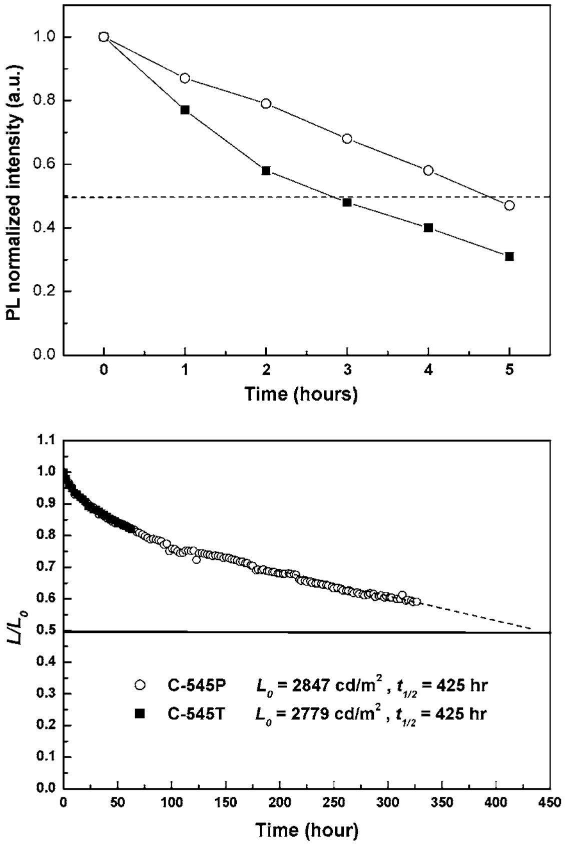

Figure 4. (a) Photostability of C-545T and **C-545P**. (b) Device operational test of C-545T and **C-545P**.

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Supporting Information Available: Synthetic procedures, spectral data, and EL-devices of **C-545P** and C-545T. This material is available free of charge via the Internet at http://pubs.as.org.

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