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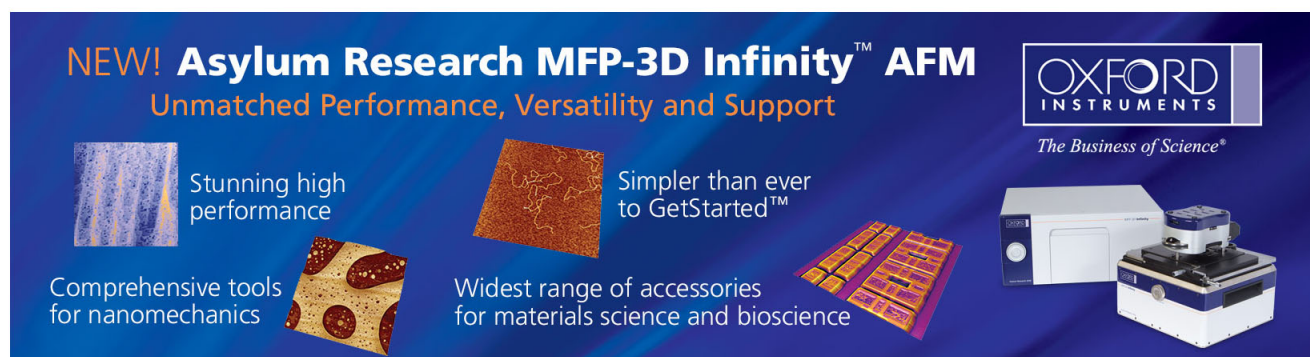
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## Efficient green organic light-emitting diodes with sterically hindered coumarin dopants

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We have discovered two sterically hindered green coumarin derivatives which showed significantly better thermal stability and overall electroluminescence (EL) performance than those of the corresponding 3-(2-benzothiazolyl)-7-(diethylamino)-2*H*-1-benzopyran-2-one (C-6) and 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). The strategic incorporation of bulky spacer *t*-butyl groups in these dopants considerably delays the onset of concentration quenching. In particular, 10-[2-(5,7-di-*t*-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) with its superb thermal stability ( $T_g=142^\circ\text{C}$ ;  $T_d=327^\circ\text{C}$ ), high luminance efficiency ( $\sim 13\text{ cd/A}$ ), good Commission Internationale d'Éclairage (CIE) coordinates ( $x=0.30$ ;  $y=0.64$ ) and a nearly flat EL efficiency dependence on drive current stands out as one of the best choice of green dopants for use in the passive-matrix organic light-emitting diode displays. © 2001 American Institute of Physics. [DOI: 10.1063/1.1420583]

Since the discovery of the multilayered organic light-emitting diodes (OLED) by Tang and co-workers at Kodak,<sup>1</sup> phenomenal progress in the areas of materials and devices have been made by many research groups throughout the world.<sup>2</sup> Due to its low power consumption, high efficiency, wide viewing angle, fast response time, and compact and lightweight nature of the device, the OLED has rapidly become one of the major flat-panel display technologies in the new century.<sup>3-5</sup> One of the key developments in the advancement of this emissive display technology can be attributed to the discovery of the guest-host doped emitter system.<sup>6</sup> This is because a single host with optimized transport and luminescent properties may be used together with a variety of highly fluorescent guest dopants leading to electroluminescence (EL) of desirable hues with high efficiencies. This doping principle has recently been extended to the exploitation of highly phosphorescent materials leading to nearly 100% internal EL efficiency.<sup>7</sup> Another advantage of the doped emitter system in OLED is the enhancement of its operational stability by transferring the electrically generated exciton to the highly emissive and stable dopant site thus minimizing its possibility for nonradiative decay.<sup>8</sup>

One of the earliest dopants used in OLED to generate efficient EL emission in the green was 3-(2-benzothiazolyl)-7-(diethylamino)-2*H*-1-benzopyran-2-one, known as C-6 (Ref. 9), which fluoresces at  $\lambda_{\text{max}}$  505 nm (EtOH) with 78% photoluminescence (PL) quantum yield.<sup>10</sup> Subsequently, it was discovered that by rigidizing the donor moiety [Et<sub>2</sub>N-] via cyclization to form the julolidine ring as in 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-

benzo[*l*]pyrano[6,7,8-*ij*]quinolizin-11-one (C-545) (Fig. 1), a more fluorescent dye (PL $\sim$ 90%) with better color could be realized by virtue of its structural coplanarity which aligns the *p*-orbital of nitrogen to overlap with the  $\pi$ -orbitals of the phenyl ring for more effective conjugation.<sup>11</sup> The enhancement of quantum efficiency is believed to be derived from diminishing the nonradiative deactivation of the excited state by reducing the internal mobility inherent in the [Et<sub>2</sub>N-] moiety of C-6. The other advantage of C-545 entails the fact

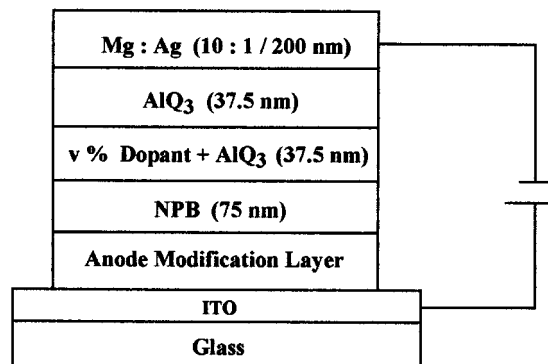
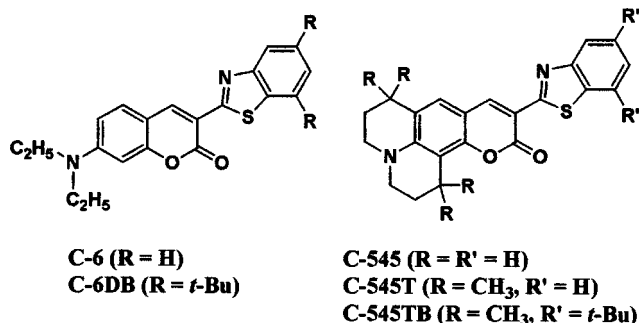


FIG. 1. EL device configuration and molecular structures of dopants.

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that its emission, now about 15 nm redshifted (to 519 nm) from that of C-6, is closer to the peak of eye sensitivity near 550 nm. Therefore, it is more suitable for display application for the “green” emitter.

The disadvantage of C-545, however, is that due to its nearly planar structure, it also has a greater tendency to aggregate in the solid state. In studies of both PL and EL of C-545 doped *tris*(8-hydroxyquinolino)aluminum (AlQ<sub>3</sub>) at a concentration >1%, a shoulder at the long-wavelength edge of the emission spectrum begins to grow which ultimately results in an undesirable hue shift and lowering of its luminance efficiency.<sup>12</sup> Further modification of the julolidyl ring in C-545 by introducing four strategically positioned methyl groups as *steric spacers* to minimize the dye–dye interaction at high dopant concentration led to the discovery of 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).<sup>13</sup> The combined advantages of high luminance efficiency, nearly perfect hue, and its resistance to concentration quenching makes C-545T an ideal candidate for doped green emitter of choice in various OLED display applications. Other notable green dopants that have been reported are quinacridone,<sup>14</sup> dimethylquinacridone,<sup>15</sup> and electrophosphorescent *fac tris*(2-phenylpyridine)iridium [Ir(ppy)<sub>3</sub>].<sup>16</sup>

However, these coumarin derivatives usually have relatively low glass transition temperature ( $T_g$ ) which will impact on the thermal stability of the devices. Furthermore, in EL applications, there is always the need to modify the dopant structure to enhance the EL efficiency in the devices to save power consumption. This is particularly important for the passive-matrix displays where the system would need to be capable of very high luminance at low voltage and have a “flat” cd/A response with respect to drive voltage. Specific substituents therefore are needed to increase the thermal stability and to enhance the EL efficiency of a given green emitting EL device based on coumarin/AlQ<sub>3</sub> emitter without significantly affecting the color of the emission.

We report in this letter, on the green dopants C-6DB and C-545TB which have all the desired attributes mentioned.<sup>17</sup> The device architectures in which to compare the EL performances of C-6DB vs C-6 and C-545TB vs C-545T along with their chemical structures are given in Fig. 1.

In the organic EL test structure, the emitting layer was AlQ<sub>3</sub> plus  $v\%$  of dopant (37.5 nm), the hole transport layer was *N,N'*-bis(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4' diamine (NPB) (75 nm) and 37.5 nm of AlQ<sub>3</sub> was evaporated as the backing electron transport layer. An additional anode modification layer which serves to lower the barrier of hole injection was inserted between the NPB layer and the indium-tin-oxide (ITO) electrode. The latter was typically 100 nm thick with a sheet resistance of about

TABLE I. Comparison of thermal properties.

Dopant	$T_g$ (°C)	$T_m$ (°C)	$T_d$ (°C)
C-6	...	209	317
C-6DB	107	286	348
C-545T	100	230	318
C-545TB	142	276	327

16 ohm/sq. Prior to the organic deposition, the ITO coated glass plate was thoroughly cleaned by scrubbing, sonication, vapor degreasing, and oxygen plasma treatment. In this work, we used two different hole injection materials in our experiments to demonstrate the advantage of dopants of C-6DB and C-545TB. In device **A**, 15 nm of copper phthalocyanine (CuPc) was used while in device **B**, CHF<sub>3</sub> plasma was used instead to modify the ITO surface.<sup>18</sup>

All EL devices were fabricated according to a protocol previously established at Kodak.<sup>19</sup> The active area of the EL device, defined by the overlap of the ITO and the cathode electrodes, was 0.1 cm<sup>2</sup>. The EL device was completed with encapsulation in a dry argon glove box. 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 thermal properties of these dopants were evaluated by differential scanning calorimetry and thermogravimetric analysis at a heating rate of 10 °C/min under nitrogen and are compared in Table I. Both dopants have higher glass transition ( $T_g$ ) and onset decomposition temperatures ( $T_d$ ) than the corresponding C-6 and C-545T. In particular, C-545TB has a  $T_g$  of 142 °C which is 42 °C higher than that of C-545T. A higher  $T_g$  is desirable for a choice of dopant materials as it will impart better operational stability to the device. Likewise, a higher  $T_d$  will also prevent dopants from thermal decomposition during resistively heated vacuum deposition.

The EL performances of device **A** and device **B** under a selected set of optimal doping concentrations of C-6 vs C-6DB and C-545T vs C-545TB are compared, respectively, in Table II. To ensure the validity of these comparisons, nearly identical coating conditions were strictly followed between each set of doping experiments. The EL cells after encapsulation in the dry box were driven with a current density of 20 mA/cm<sup>2</sup>. In general, the CHF<sub>3</sub> plasma treated ITO which has better hole injection characteristics has a lower drive voltage than that of CuPc. In both type of devices, the di-(*t*-butyl)-substituted dopants, C-6DB and C-545TB, produced more light under the similar drive conditions than C-6 and C-545T. This is reflected in the advantage of the luminance efficiency gain of 1.2–1.4 cd/A in device **A** and 2.4–2.7 cd/A in device **B**. In power consideration, the gains are

TABLE II. Comparison of EL performances of device **A** and **B** shown in parenthesis driven at 20 mA/cm<sup>2</sup>.

Dopant	$v$ %	V	cd/m <sup>2</sup>	cd/A	Im/W	CIE <sub>x</sub>	CIE <sub>y</sub>
C-6	0.8 (0.7)	7.9 (9.3)	1447 (1615)	7.2 (8.1)	2.9 (2.7)	0.29 (0.28)	0.63 (0.63)
C-6DB	0.8 (0.7)	8.2 (11.8)	1683 (2150)	8.4 (10.8)	3.2 (2.9)	0.29 (0.28)	0.62 (0.64)
C-545T	1.0 (1.0)	6.8 (11.1)	1748 (2364)	8.7 (10.5)	4.1 (3.3)	0.33 (0.30)	0.63 (0.65)
C-545TB	1.0 (1.0)	6.9 (11.6)	2014 (2585)	10.1 (12.9)	4.6 (3.5)	0.32 (0.30)	0.63 (0.64)

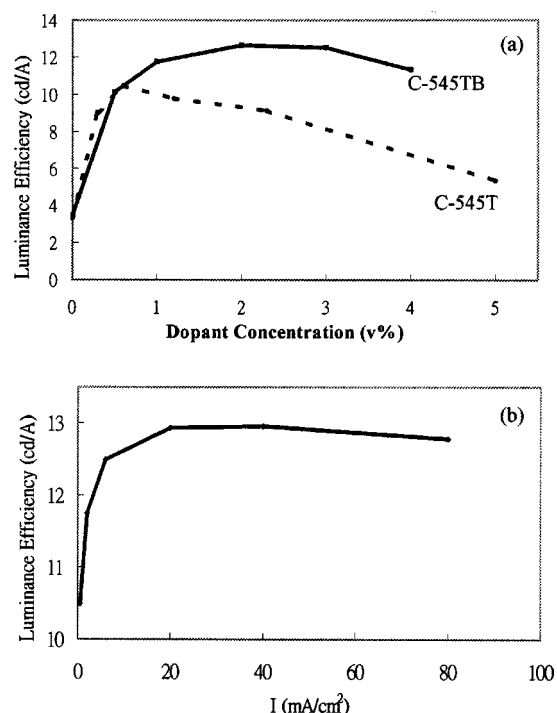


FIG. 2. (a) Luminance efficiency vs doping concentration of C-545T and C-545TB and (b) luminance efficiency of C-545TB vs current density.

also significant with 0.3–0.5 lm/W in device **A** and 0.2 lm/W in device **B**. Another attractive attribute of these dopants is the fact that these gains in luminance do not significantly change their 1931 Commission Internationale d'Éclairage (CIE) coordinates as exemplified in Table II. From these data, it is concluded that dopant C-545TB offers the best overall luminance efficiency, power efficiency, and the most saturated green with CIE  $x=0.32$ ;  $y=0.63$  in device **A** and CIE  $x=0.30$ ;  $y=0.64$  in device **B** as a doped emitter in AlQ<sub>3</sub> for OLED display applications.

The doping concentration in AlQ<sub>3</sub> and luminance efficiency dependency curves for C-545T and C-545TB in device **A** are compared in Fig. 2(a). Dopant C-545TB with extra steric spacers is apparently less sensitive to concentration quenching than C-545T. The luminance efficiency of C-545T begins to drop after 1% while the di-(*t*-butyl)-substituted C-545TB derivative remains robust over a wide range of doping concentration between 1–4%. Using CuPc (15 nm) as the injection layer, the turn-on voltage of C-545TB doped emitter is about 6.6 V and at 17.5 V, the luminance is well over 10 000 cd/m<sup>2</sup>.

An additional advantage of C-545TB can be found in Fig. 2(b) from its nearly flat response of luminance efficiency (cd/A) with respect to a wide range of drive current conditions from 20 to 80 mA/cm<sup>2</sup> at an optimal doping concentration of about 1%. This is particularly desirable for the

passive-matrix displays where the system would need to be capable of very high luminance at low voltage and have a flat cd/A response with respect to drive voltage.

In conclusion, we report on two sterically hindered green dopants, C-6DB and C-545TB, which showed significantly better thermal stability as well as overall EL performance than those of the corresponding C-6 and C-545T. In particular, dopant C-545TB with its superb thermal stability, high luminance efficiency, good colorimetry, and a nearly flat EL efficiency dependence on drive current stands out as an outstanding choice of green dopants for use in the passive-matrix OLED displays.

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