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Author(s)	Xiang, HF; Yu, SC; Che, CM; Lai, PT
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Efficient white and red light emission from GaN/*tris*-(8-hydroxyquinolato) aluminum/platinum(II) *meso*-tetrakis(pentafluorophenyl) porphyrin hybrid light-emitting diodes

Hai-Feng Xiang
Department of Chemistry and the HKU-CAS Joint Laboratory on New Materials, and Department of Electrical and Electronic Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, People's Republic of China

Sze-Chit Yu and Chi-Ming Che[a)]
Department of Chemistry and the HKU-CAS Joint Laboratory on New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, People's Republic of China

P. T. Lai
Department of Electrical and Electronic Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, People's Republic of China

We report efficient white and red light emission from GaN light-emitting diode (LED)/*tris*-(8-hydroxyquinolato) aluminum (Alq_3)/platinum(II) *meso*-tetrakis(pentafluorophenyl) porphyrin ($PtF_{20}TPP$) hybrid LEDs. Alq_3 was employed to enhance the efficiency of red and white luminescence conversion (LC) LEDs through energy transfer from Alq_3 to $PtF_{20}TPP$. In the white LC-LED, an intense, highly pure white-light emission with CIE_1931 coordinates at $x=0.32$ and $y=0.31$ is obtained. The LC-LEDs in this work have relatively high efficiencies, 3.3% for white LC-LED and 4.0% for red LC-LED. The color temperature (T_c), color rendering index (R_a) and luminous efficiency (η_L) of the white LC-LED at 20 mA are 6800 K, 90.6 and 10 lm/W, respectively. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1604192]

Recent progress in GaN-based technology has led to the development of bright green, blue, and shorter-wavelength light-emitting diodes (LEDs).[1–5] White-light LED is particularly desirable as an alternative solid-state lighting source. Using blue or near-ultraviolet (*n*-UV) light GaN-LEDs as the primary light source, longer-wavelength light emission can be achieved by luminescence conversion (LC) of organic or inorganic dyes.[2,6–14] The underlying principle is luminescence down conversion (Stokes shift) of the dyes from shorter-wavelength to longer-wavelength emission.

Previous works showed that white-light LED can be fabricated using GaN/conjugated polymer,[6,7] or GaN/low-molar-mass organic[2,8–9] or inorganic dye [yttrium–aluminum–garnet (YAG)] hybrid materials.[8,10–14] The conjugated polymers are photooxidatively and thermally unstable,[7] and the inorganic yellow phosphor (YAG) shows insufficient red emission and low color rendering index (R_a).[13,14] In this letter, we report the use of the red dye platinum(II) *meso*-tetrakis(pentafluorophenyl) porphyrin ($PtF_{20}TPP$), green dye *tris*-(8-hydroxyquinolato) aluminum (Alq_3) and GaN-LEDs to achieve white and red LC-LEDs. The chemical structures of the dyes are depicted in Fig. 1.

Commercial *n*-UV GaN-LED, LC503MUV1-30Q (COTCO), was used as the light pump in the experiments [Fig. 2(a)]. The GaN-LED exhibits a sharp emission at λ_{max} 393 nm (CIE_1931 chromaticity coordinates: $x=0.17$, $y=0.02$) with an efficiency (light power output/electric power input) of 11%. Beyond the threshold current of 3.4 mA, the output power of the GaN-LED increases linearly with increasing current input. In this work, the red dye $PtF_{20}TPP$[15–17] was chosen for LED applications[18] because: (1) it has good solubility in many organic solvents such as chloroform (1.0 dm^3 chloroform can dissolve more than 20 mg $PtF_{20}TPP$); (2) it shows an intense red phosphorescence [photoluminescence (PL)] quantum yield of ~12% in dichloromethane; with full width at half maximum (FWHM) of 26 nm; CIE_1931 of $x=0.72$, $y=0.28$ [Fig. 2(b)]; (3) there is a strong UV/Vis absorption in hexane (Soret band [$\lambda_{max}=390$ nm, $\varepsilon=2.6\times10^5$ dm^3 mol^{-1} cm^{-1}]; $Q(1,0)$ [$\lambda_{max}=504$ nm, $\varepsilon=1.6\times10^4$ dm^3 mol^{-1} cm^{-1}] and $Q(0,0)$ [$\lambda_{max}=538$ nm, $\varepsilon=1.5\times10^4$ dm^3 mol^{-1} cm^{-1}]); (4) there is a large Stokes shift between the absorption and emission spectra; (5) it has good photooxidative stability [Fig. 3(c)]; (6) it
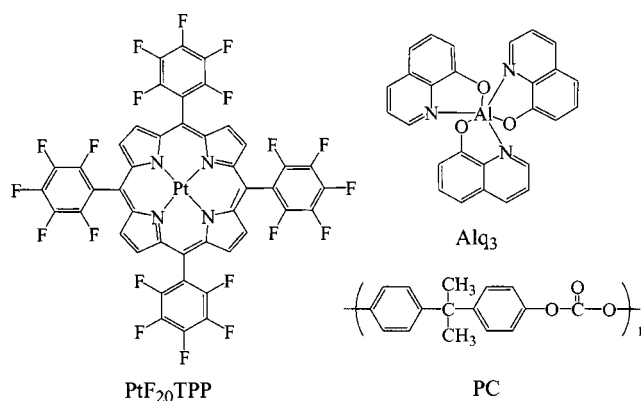

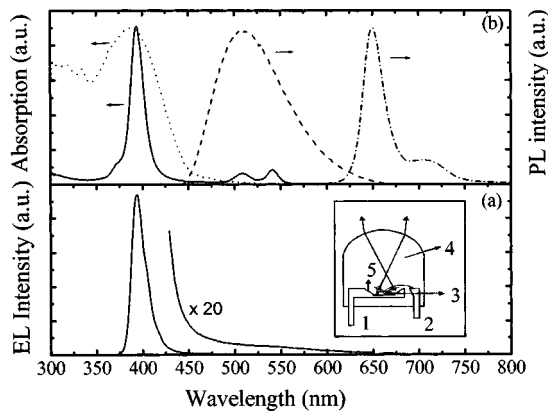FIG. 1. The chemical structures of $PtF_{20}TPP$, Alq_3, and PC.

FIG. 2. (a) The EL spectrum of *n*-UV GaN-LED. Inset: schematic diagram of the *n*-UV GaN-LEDs in a transparent epoxy package: (1) anode post, (2) cathode post, (3) GaN chip, (4) epoxy lens, and (5) reflector cup. (b) The absorption spectra of $PtF_{20}TPP$ (solid line) and Alq_3 (dotted line); the PL emission spectra of $PtF_{20}TPP$ (dash-dotted line) and Alq_3 (dashed line).

has high thermal stability (decomposition temperature T_d at 413 °C; there is no change in PL emission intensity after heating the $PtF_{20}TPP$ thin film at 120 °C in air for 1000 h); (7) the thin-film PL quantum yield of $PtF_{20}TPP$ is probably larger than that in solution because the rotation of phenyl groups provides a nonradiative relaxation pathway for the triplet excited state of $PtF_{20}TPP$; this relaxation would possibly be frozen in solid thin film.[17]

All thin films were prepared by spin-coating method in the following manner: (a) dissolving the dyes in chloroform along with poly(bisphenol A carbonate) (PC) (Fig. 1) and (b) dispersing the solution mixture on quartz plate, spinning the plate and baking the film at 80 °C under vacuum for 12 h to form a transparent matrix film. The thickness of the film was approximately 500 nm. All the measurements were performed at ambient temperature in air. On the other hand, red and white LC-LEDs were prepared by dip-coating method. In contrast to the reported "double layers method," [6] $PtF_{20}TTP$, Alq_3 and PC were dissolved in chloroform to form a single layer film on the epoxy of the LED. The concentrations of the dyes were adjusted to fine tune the emission color of the hybrid LC-LEDs. The output power of the LEDs was measured by laser power monitor (OPHIR).

As depicted in Fig. 2(b), the Soret absorption band ($\lambda_{max}=394$ nm as thin film) of $PtF_{20}TPP$ overlaps with the electroluminescence (EL) spectrum of *n*-UV GaN-LED ($\lambda_{max}=394$ nm). This overlap provides a channel for efficient luminescence conversion. At first, we prepared red LC-LED with $PtF_{20}TPP$ and *n*-UV GaN-LED only. This LED shows an impure red color emission, as shown in Fig. 3(a). The surplus of *n*-UV emission from GaN-LED affects the purity of red light, and the CIE_1931 chromaticity is shifted to $x=0.50$ and $y=0.24$. We have then tried to optimize the LED performance in two ways. The first attempt was to increase the thickness of dip-coating film and concentration of $PtF_{20}TPP$. However, the efficiency of LED was found to decrease as a result of self-quenching and self-absorption at high $PtF_{20}TPP$ concentration. The second attempt was to choose a dye that can absorb the high-energy emission from *n*-UV GaN-LED and then transfer the absorbed energy to the red phosphorescent dye $PtF_{20}TPP$. We found that Alq_3 is a good material for this purpose. The absorption spectrum of
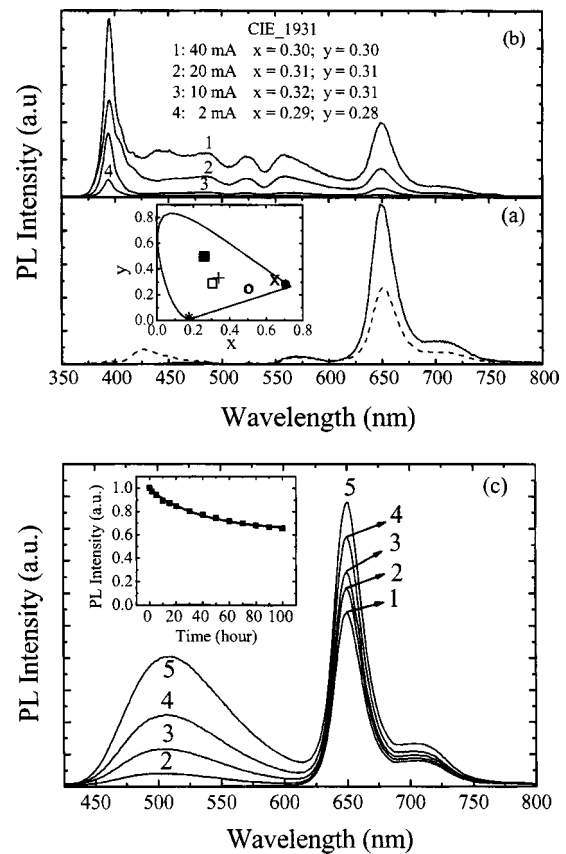

FIG. 3. (a) Emission spectra of the red LC-LED (solid line) doped with Alq_3 and without Alq_3 (dashed line). Inset: CIE_1931 chromaticity diagram, with coordinates corresponding to emission of the *n*-UV GaN LED (*), Alq_3 thin film (■), $PtF_{20}TPP$ thin film (●), red LC-LED doped with Alq_3 (×), red LC-LED without Alq_3 (○), the white LC-LED (□), and ideal pure white emission (+). (b) Emission spectra and CIE_1931 chromaticity coordinates of the white LC-LEDs under different applied currents. (c) PL spectra of $PtF_{20}TPP$ (1.0% in PC) as thin-film doped with Alq_3 (excited at 394 nm); (1) 1:0, (2) 1:2, (3) 1:5, (4) 1:10, (5) 1:20 ($PtF_{20}TPP:Alq_3$, by weight). Inset: photooxidative measurement of $PtF_{20}TPP$ film under irradiation of 1 mW/cm² at 394 nm in air at ambient temperature (signal detected at 650 nm).

Alq_3 overlaps with the EL spectrum of *n*-UV GaN-LED. In addition, the PL emission of Alq_3 overlaps with the $Q(1,0)$ band ($\lambda_{max}=509$ nm as thin film) and $Q(0,0)$ band ($\lambda_{max}=541$ nm as thin film) of $PtF_{20}TPP$ (Fig. 2). The PL spectra of $PtF_{20}TPP$ thin films doped with various concentrations of Alq_3 are shown in Fig. 3(c). Increasing the ratio of Alq_3 to $PtF_{20}TPP$ enhances the intensity of the red photoluminescence from $PtF_{20}TPP$. The optimal ratio of $PtF_{20}TPP$ to Alq_3 (by weight) is 1:5. No surplus of *n*-UV emission from GaN-LED can be observed under this condition. The high-energy emission from GaN-LED is effectively converted to low-energy emission through luminescence conversion. The efficiency of the red LC-LED has been found to be remarkably improved by Alq_3. Also, we successfully obtained a saturated red-light LED with CIE_1931 coordinates at $x=0.65$ and $y=0.32$ [Fig. 3(a)]. The CIE chromaticity coordinates of the red LC-LED are independent of current inputs (from 5 to 40 mA).

Intense high-purity white light emission has also been achieved by a similar fabrication method. By varying the ratio of $PtF_{20}TPP$ to Alq_3 from 1:5 to 1:40 (by weight) and the $PtF_{20}TPP$ concentrations in poly(bisphenol A carbonate)

from 5.0% to 1.0%, the *n*-UV EL emission from GaN-LED, the green emission from Alq_3, and the red emission from $PtF_{20}TPP$ combine to give white emission. The emission from the white LC-LED shows highly pure white color of CIE_1931 coordinates at $x = 0.32$ and $y = 0.31$, which is close to the ideal pure white CIE_1931 coordinates at $x = 0.33$ and $y = 0.33$ [Fig. 3(b)]. The CIE_1931 coordinates of our white LC-LED change slightly from (0.29, 0.28) to (0.32, 0.31) upon varying the input current from 2 to 40 mA. Under a forward bias of 20 mA, the color temperature (T_c), color rendering index (R_a) and luminous efficiency (η_L) of the white LC-LED are 6800 K, 90.6 and 10 lm/W, respectively. Compared to the commercial white LED (blue LED (~ 460 nm) + yellow phosphor), our white LED shows several advantages: (1) the luminous efficiency augments linearly with increasing input current (for commercial LED, the output signal of the blue-color emission tends to saturate at high input current);[14] (2) the combination of *n*-UV, green and red colors leads to lower T_c and higher R_a values; and (3) the CIE coordinates change only slightly with varying driving current [Fig. 3(b)]. Narukawa and co-workers recently reported a phosphor-conversion white LED using InGaN *n*-UV chip, blue and yellow phosphors.[12] In this work, we employed two organic phosphors instead of inorganic materials to fabricate the white LC-LED. The red dye $PtF_{20}TPP$ was used to generate the red component for white emission; a higher *Ra* value (90.6) and highly pure white emission have been achieved.

In the case of a hybrid LED with a single layer, the conversion efficiency (the ratio of the number of photons emitted to the number of photons from the *n*-UV pump) is given by

$$\eta_c = f_\alpha \eta_{PL} + (1 - f_\alpha) = 1 - f_\alpha(1 - \eta_{PL}), \qquad (1)$$

where f_α is the fraction of pump light absorbed by the dye film; η_{PL} is the PL quantum efficiency of the dye film; and $(1 - f_\alpha)$ is the fraction of residual light from GaN-LED. For the white LC-LED with two dyes in a single film, due to the energy transfer from Alq_3 to $PtF_{20}TPP$, Eq. (1) is modified to

$$\eta_c = f_{\alpha,r} \eta_{PL,r} + f_{\alpha,g} f_t \eta_t + (f_{\alpha,g} - f_{\alpha,g} f_t) \eta_{PL,g}$$
$$+ (1 - f_{\alpha,r} - f_{\alpha,g}) = 1 - f_{\alpha,r}(1 - \eta_{PL,r})$$
$$- f_{\alpha,g}(1 - \eta_{PL,g}) - f_{\alpha,g} f_t(\eta_{PL,g} - \eta_t), \qquad (2)$$

where $f_{\alpha,r}$ and $f_{\alpha,g}$ are the fractions of pump light absorbed by the red dye film and the green dye film, respectively; $\eta_{PL,r}$ and $\eta_{PL,g}$ are the PL quantum efficiencies of the red dye film and green dye film, respectively; f_t is the fraction of energy transfer from the green dye film to the red dye film; and η_t is the quantum efficiency of the red dye film caused by energy transfer from the green dye film. For the red LC-LED, all emission from the *n*-UV GaN LED is absorbed ($f_{\alpha,r} + f_{\alpha,g} = 1$) and no emission from the green dye film ($f_t = 1$) can be observed. Therefore, Eq. (2) is simplified to

$$\eta_c = f_{\alpha,r} \eta_{PL,r} + f_{\alpha,g} \eta_t. \qquad (3)$$

The *n*-UV GaN LED shows a power output of 8.0 mW at a current of 20 mA with 11% EL efficiency. Using the *n*-UV LED as pumping source, our red LC-LED has a power output of 3.0 mW with 4.0% efficiency at 20 mA. This is more comparable to the literature value of 1.9% efficiency for InGaN/conjugated polymer hybrid LEDs.[6] The *n*-UV-to-red conversion efficiency is 36%. However, the efficiency of our red LC-LED is lower than that of AlGaAs-based red LED (10%).[19] This is possibly due to the absence of LED encapsulation and low efficiency of *n*-UV LED (11% EL efficiency). Under same forward bias at 20 mA, our white LC-LED shows a power output of 2.6 mW with 3.3% efficiency; and the *n*-UV-to-white conversion efficiency is 30%. The luminous efficiency of 10 lm/W is obtained which is lower than that reported by Narukawa *et al.*;[12] this is presumably due to the low luminous efficiency *n*-UV LED (0.90 lm/W). The emissions from our unpackaged red and white LC-LEDs demonstrated 50% degradation after 1000 h at ambient temperature in air. We anticipate that the lifetime and brightness of the LC-LEDs described in this work can be improved by encapsulation of the dyes at the top of the GaN chip on the reflector cup using epoxy material.[8,9] Encapsulation of LED can reduce viewing-angle dependence because the epoxy material can be used as a lens to focus the light.

In conclusion, we have demonstrated a strategy to obtain intense, highly pure white and red emissions from GaN-LED/Alq_3/$PtF_{20}TPP$ hybrid LC-LEDs. The white LED has high color rendering index (90.6) at 20 mA. This provides an impetus development for designing effective and highly pure red and white LEDs by using organic materials.

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