Chem. Mater. **1999,** *11,* 3709−3713

Efficient, Saturated Red Organic Light Emitting Devices Based on Phosphorescent Platinum(II) Porphyrins

Raymond C. Kwong,[†] Scott Sibley,[‡] Timur Dubovoy,[‡] Marc Baldo,[§]
Stephen R. Forrest,[§] and Mark E. Thompson*,[†]

Department of Chemistry, University of Southern California, Los Angeles, California 90089; Department of Chemistry, Goucher College, Baltimore, Maryland 21204-2794; and Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544

Received October 7, 1999

Two new platinum(II) porphyrins have been synthesized and their luminescent properties have been studied. The platinum porphyrins exhibited strong phosphorescence in the red with narrow line widths. When they were doped into aluminum(III) tris(8-hydroxyquinolate) (AlQ_3) in the electron-transporting and -emitting layer of an organic light-emitting device, energy transfer occurred between the host AlQ_3 and the platinum porphyrin. Bright saturated red emission with high efficiency at low to moderate current density has been achieved. In the high current regime, the electroluminescence efficiency decreased and the perceived emission color blue shifted as a result of mixed emission from the platinum porphyrin and AlQ_3. This current dependence was due to the saturation of triplet emissive sites, because of the long-lived phosphorescence state of the platinum porphyrin complex.

Introduction

Achieving saturated red emission with high quantum and luminous efficiencies remains a challenge in the field of organic electroluminescence. Red organic light emitting diodes (OLEDs) are usually fabricated by doping red dyes into a suitable host.[1,2] The most commonly used host for this purpose is aluminum(III) tris(8-hydroxyquinolate) (AlQ_3). Doping a small amount (∼1%) of a red laser dye such as DCM or DCJ in AlQ_3 gives high quantum efficiency (2.3%, photons/electrons), although the emission color appears orange.[3] Increasing the doping concentration to 2% results in red emission due to polarization effects,[4] but the efficiency of the devices decreases significantly due to enhanced self-quenching. DCLJ, a sterically bulky derivative of DCJ, has been synthesized to reduce the extent of self-quenching at high level doping.[5] The efficiency of the based DCJT device is relatively high (∼2.5%); however, the red color emission still suffered from a broad bandwidth. Saturated red can also be achieved by doping tetraphenylporphyrin (TPP) into AlQ_3, but the quantum efficiency remained low (∼0.1%).[6] Another approach is to use Eu(III) complexes as dopants.[7,8] Vapor deposited devices with Eu(III) complexes such as $Eu(DBM)_3(Phen)$[9] show a sharp emission band at 620 nm which is typical of the $^5D_0 \rightarrow {}^7F_2$ transition of the trivalent lanthanide ion.[10] The chromaticity of Eu(III) complex-doped devices is satisfactory, with a quantum efficiency of 0.8%. The most promising candidate for red color display to date is platinum(II) octaethylporphyrin (PtOEP) which has shown exceptionally high efficiency (∼7%) at low injection current.[11,12] Devices with PtOEP doped into AlQ_3 showed narrow emission centered at 650 nm, resulting in a saturated red color. Efficiency as high as 1.3% was achieved, at a luminance of 100 cd/m^2, for AlQ_3-doped OLEDs and 1.9%, in optimized OLEDs.[13] PtOEP has also been used as a phosphorescent dye in polymer LEDs to achieve saturated red emission.[14] Both Eu(III) and Pt(II) complexes are phosphorescent, unlike most other dyes used in OLEDs, which are fluorescent.[2] Using triplet-based emitting centers in OLEDs eliminates the 25% maximum internal quantum efficiency, which is the expected singlet

---

* To whom correspondence should be addressed. E-mail: met@usc.edu. Phone: (213)740−6402. Fax: (213)740−8594.

[†] University of Southern California.

[‡] Goucher College.

[§] Princeton University.

(1) Chen, C. H.; Shi, J.; Tang C. W. *Macrolmol. Symp.* **1997**, *125*, 1. Sibley, S. P.; Thompson, M. E.; Burrows, P. E.; Forrest, S. R. *Optoelectronic Properties of Inorganic Compounds*; Roundhill, D. M., Fackler, J., Eds; Plenum Publishing Co.: New York, 1999; Chapter 2. Rothberg, L. J.; Lovinger, A. J. *J. Mater. Res.* **1996**, *11*, 3174.

(2) Shoustikov, A. A.; You Y.; Thompson, M. E. *IEEE J. Selected Top. Quantum Electron.* **1998**, *4*, 3.

(3) Tang. C. W.; Van Slyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610.

(4) Bulovic, V.; Shoustikov, A.; Baldo, M. A.; Bose, E.; Kozlov, V. G.; Thompson, M. E.; Forrest, S. R. *Chem. Phys. Lett.* **1998**, *287*, 455.

(5) Tang, C. W. *Dig. Soc. Information Display Int. Symp.* **1996**, *27*, 181.

(6) Burrows, P. E.; Forrest, S. R.; Sibley, S. P.; Thompson, M. E. *Appl. Phys. Lett.* **1996**, *69*, 2959.

(7) Kido, J.; Nagai, K.; Okamato, Y.; Skotheim, T. *Chem. Lett.* **1991**, 1267.

(8) Kido, J.; Nagai, K.; Ohashi, Y. *Chem. Lett.* **1990**, 657.

(9) Kido, J.; Hayase, H.; Hongawa, K.; Nagai, K.; Okuyama, K. *Appl. Phys. Lett.* **1994**, *65*, 2124.

(10) . Sabbatini, N.; Guardigli, M.; Lehn, J.-M. *Coord. Chem. Rev.* **1993**, *123*, 201.

(11) Thompson, M. E.; Shoustikov, A.; You, Y.; Sibley, S.; Baldo, M.; Koslov, V.; Burrows, E. P.; Forrest, S. R. *MRS Abstract*, G2.4, Spring Meeting, 1998.

(12) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151.

(13) O'Brien, D. F.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett* **1999**, *74*, 442.

(14) Cleave, V.; Yahioglu, G.; Barny, P. L.; Friend, R. H.; Tessler, N. *Advanced Mater.* **1999**, *11*, 285.

10.1021/cm9906248 CCC: $18.00

exciton fraction achieved by electrical injection.[15,16] This is a benefit of all phosphorescence-based OLEDs and gives them the potential of having much higher quantum efficiencies than fluorescence-based ones. The energy of the photophysical transition for lanthanide complexes is determined by the energetics of the metal ion,[17] while the emission in platinum(II) porphyrins is largely ligand-based.[18] Therefore, by chemical modification of the porphyrin framework, the luminescent properties of the Pt(II) complex can be fine-tuned. To further explore the concept of using phosphorescent dyes in OLEDs, two new platinum(II) porphyrins have been synthesized and studied. We report here our work in utilizing them as red phosphorescent dyes in OLEDs with improved quantum and luminous efficiencies.

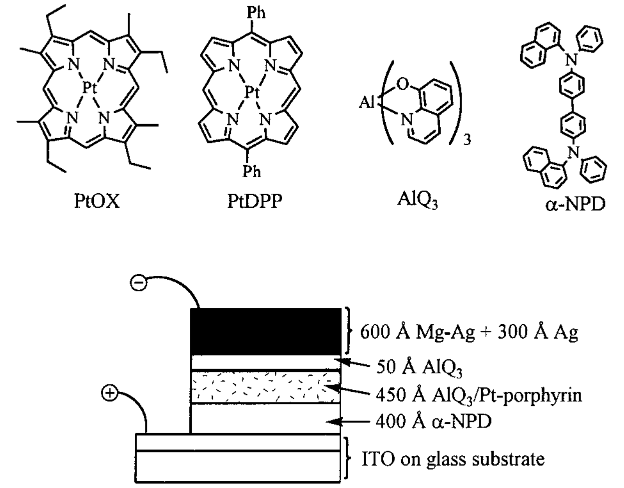
Experimental Section

Materials. All reagents and anhydrous solvents were purchased from Aldrich and used without further purification. AlQ_3[19] and 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (α-NPD)[20] were synthesized according to the literature procedures and purified by vacuum sublimation. 5,15-Diphenylporphyrin (abbreviated here as H_2DPP) was synthesized from a condensation−cyclization reaction with 2,2′-dipyrrolemethane and benzaldehyde as described by Therien et al.[21] 2,2′-Dipyrrolemethane was synthesized by a three-step procedure starting with pyrrole and thiophosgene.[22] Etioporphyrin III (abbreviated here as H_2OX) was synthesized by reducing the commercially available protoporphyrin IX (isolated from ox hematin) through a one-step hydrogenation−decarboxylation reaction.[23] The platinum complexes PtDPP and PtOX were synthesized by refluxing the corresponding free base in degassed benzonitrile with $PtCl_2$. Typical procedures were as follows: One gram of the free base and $PtCl_2$ (2 equiv) were suspended in 100 mL of anhydrous benzonitrile. The mixture was then purged with N_2 as it was slowly heated to 160 °C. It was then brought to reflux under N_2 until there was no free base left as revealed by TLC. The mixture was then cooled to room temperature and the solvent was removed by vacuum distillation. The crude product left behind was then dried completely and purified by sublimation at 300 °C at $<10^{-4}$ Torr. Both Pt(II) complexes were characterized spectroscopically and by elemental analysis:

PtDPP. ^1H NMR: δ 10.15 (s, 2H), 9.21 (dd, 4H, $J_1 = 12$ Hz, $J_2 = 7.5$ Hz), 8.93 (dd, 4H, $J_1 = 12$ Hz, $J_2 = 7.5$ Hz), 8.18 (m, 4H), 7.77 (m, 6H). MS (EI): m/z (relative intensity) 655 (M^+, 100), 577 (30), 326 (50), 288 (35). UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 388 (5.33), 499 (4.15), 530 (4.04). Elemental analysis: calculated C, 58.62; H, 3.07; N, 8.55; Pt, 29.76; found C, 58.35; H, 3.08; N, 8.37. Pt, 29.90.

PtOX. ^1H NMR: δ 9.98 (s, 4H), 3.99 (q, 8H, $J = 8$ Hz), 3.55 (s, 12H), 1.84 (t, 12H, $J = 8$ Hz), MS (EI): m/z (relative intensity) 671 (M^+, 100), 656 (90), 642 (50), 625 (35), 611 (28). UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 380 (5.30), 500 (4.22), 535 (4.62). Elemental analysis: calculated C, 57.22; H, 5.40; N, 8.34; Pt, 29.04; found C, 57.15; H, 5.20; N, 8.18; Pt, 29.34.

Scheme 1. OLED Device Structure and Chemicals Structures of the Compounds Used



Photoluminescence. Quantum efficiency measurements were carried out at room temperature in a toluene−DMF solution (degassed by a freeze−pump−thaw cycle, 20 times) with excitation at 500 nm. All samples were adjusted to give the same absorbance of 0.038 at 500 nm. Estimation was based on ZnTPP in benzene as the reference with a 0.03 quantum efficiency at 298 K.[24] Quantum efficiency measurements were obtained using an Aminco-Bowman Series 2 Luminescence spectrometer. Steady-state emission experiments at room temperature were performed on a PTI QuantaMaster Model C-60 Spectrofluorometer. Phosphorescence lifetime measurements were performed on the same fluorimeter equipped with a microsecond Xe flash-lamp. There were three types of samples studied and they were prepared as follows: First, the degassed toluene/DMF solution sample was of the same concentration as that used for the quantum yield measurement. The second sample was prepared by doping the porphyrin into AlQ_3 by vacuum vapor deposition on glass substrates with rates adjusted to give the same doping level as in the emitting layer of the OLED, i.e., 6 mol %. The third sample was prepared by spin-coating a 0.5% porphyrin/polystyrene (w/w) solution in anhydrous toluene on glass slides. The fluorimeter chamber was kept under nitrogen throughout the lifetime measurement to prevent the complication of oxygen quenching. The excitation was set at 390 nm for both porphyrins while the decay was monitored at 648 and 628 nm for PtOX and PtDPP, respectively.

Device Fabrication and Testing. Patterned anode contacts were made from commercially available ITO-coated glass (100 $\Omega/\square$) in our laboratory using a photolithographic technique to form circular anodes with 1 mm radii. In a vacuum chamber at pressure $<1.0 \times 10^{-5}$ Torr, 400 Å of α-NPD as the hole-transporting layer; 450 Å of dye-doped AlQ_3 as the electron-transporting and -emitting layer; 50 Å of AlQ_3 as electron-injection layer; and a cathode composed of 600 Å of Mg−Ag (10:1) capped with 300 Å of Ag, were sequentially deposited onto the substrate to give the device structure shown in Scheme 1. The platinum porphyrin dye and AlQ_3 were co-deposited with rates of ∼0.1 and ∼1.1 Å/s, respectively, to give a doping level of 6 mol % in the emitting layer. Device current−voltage and light intensity characteristics were measured using a Keithley 2400 SourceMeter/2000 Multimeter coupled to a Newport 1835-C Optical Meter using the LabVIEW program by National Instruments.

Result and Discussion

Photoluminescence. The room-temperature photoluminescence spectra of PtOX and PtDPP are shown in

---

[15] Rothberg, L. J.; Lovinger, A. J. *J. Mater. Res.* **1996**, *11*, 3174.

[16] Pope, M.; Swenberg, C. E. *Electroinc Processes in Organic Crystals*; Clarendon Press: Oxford, 1982.

[17] Richardson, F. S. *Chem. Rev.* **1982**, *82*, 541.

[18] Smith, K. M. *Porphyrins and Metalloporphyrins*; Elsevier Press: New York, 1975.

[19] Schmidbauer, H.; Lettenbauer, J.; Kumberger, O.; Lachmann, J.; Muller, G. Z. *Naturforsch.* **1991**, *46b*, 1065.

[20] Drive, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217. Wolre, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215.

[21] DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. *J. Org. Chem.* **1993**, *58*, 5983.

[22] Chong, R.; Clezy, P. S.; Liepa, A. J.; Nichol, A. W. *Aust. J. Chem.* **1969**, *22*, 229.

[23] Kämpfen, U.; Eschenmoser, A. *Hel. Chim. Acta* **1989**, *72*, 185.

[24] Seybold, P. G. and Gouterman, M, *J. Mol. Spectrosc.* **1969**, *31*, 1.

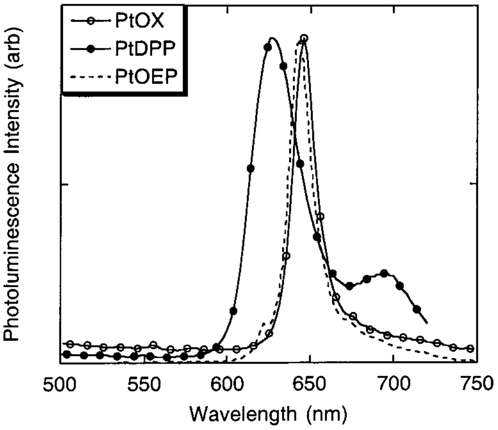


Figure 1. Room-temperature photoluminescence spectra of PtOX, PtDPP, and PtOEP in polystyrene matrix, excited at 390 nm.

Figure 1. A narrow emission peak (26 nm full width at half-maximum intensity) centered at a wavelength of 648 nm was obtained for PtOX, similar to other octaalkylporphyrins.[18] A wider emission centered at 630 nm with a weak second band at 695 nm is observed for PtDPP, characteristic of arylporphyrins.[18] The emission spectra are essentially the same when exciting at either the Soret band (∼390 nm) or the Q-bands (500−540 nm). The luminescence quantum efficiencies measured for the deoxygenated toluene/DMF solutions at room temperature were found to be 0.45, 0.44, and 0.16 for PtOEP, PtOX, and PtDPP, respectively, with error bars of roughly 20%. The quantum efficiency of PtOX is essentially the same as PtOEP. This similarly is not surprising since the only difference in the structures of PtOEP and PtOX is in the alkyl groups at the β-positions of the porphyrin ring. These alkyl groups are not conjugated to the porphyrin system and consequently have little electronic communication to the π-system. On the other hand, the quantum efficiency of PtDPP is significantly lower. We attribute this to the effect of the phenyl groups at the *meso* positions which are conjugated to the π-system. The rotational of the phenyl groups presumably induces nonradiative decay pathways of the excited states that are not present in either PtOX or PtOEP.[25] Moreover, the *beta* and the *meso* substitution patterns in porphyrins may have different ground-state and excited-state symmetries,[26] which could also affect the radiative and nonradiative decay rates.

Photoluminescence decay studies were carried out to estimate the lifetimes of the excited states. The lifetimes of the toluene/DMF solution samples at room temperature were found to be 83, 76, and 34 μs for PtOEP, PtOX, and PtDPP, respectively. The PtOEP and PtOX lifetimes are the same within the error limits of the measurement (± 3 μs). The long lifetimes of the excited states of these Pt porphyrins clearly indicate their triplet nature. The trend observed in lifetimes is similar to that observed for the quantum yields, suggesting that the radiative rates for the three complexes are very similar. Thin film samples were prepared by spin-coating a solution of the porphyrin and polystyrene onto glass slides. The solution was degassed by thoroughly purging with nitrogen prior to spin-coating, and the measurements were performed in a nitrogen flushed chamber to minimize oxygen quenching. The porphyrin concentration was kept under 1 wt % in the polystyrene matrix to minimize concentration quenching. Lifetimes of 92 and 95 μs were measured for PtOX and PtDPP, respectively. The similarity of the lifetimes for PtOX and PtDPP in polystyrene suggest that the quantum yields for the two films are very similar, in direct contrast to the quantum efficiencies and lifetimes measured in solution. Phenyl group rotation may be responsible for the nonradiative relaxation in PtDPP, which would be active in solution, but may be frozen out in the solid polystyrene thin film. The luminescent lifetimes of PtOX and PtDPP doped into a solid film of AlQ_3 were also measured. The platinum porphyrins were doped into AlQ_3 at 6 mol %, and the films were kept under nitrogen during the lifetime measurement. The measured lifetimes for PtOX and PtDPP in AlQ_3 are 39 and 21 μs, respectively. The lifetime measured for PtOEP under identical conditions was 37 μs.[12]

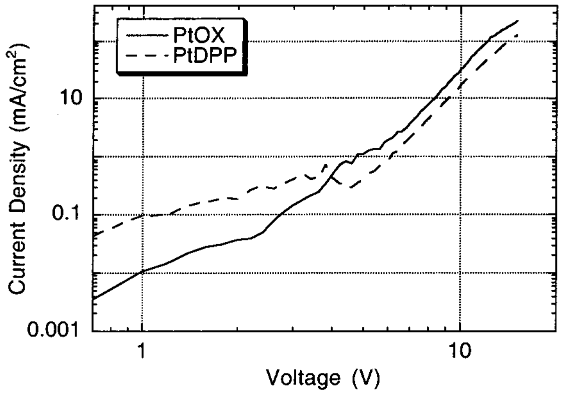


Figure 2. Current−voltage profiles of the PtOX and PtDPP OLEDs.

Electroluminescence. The OLED device structure is a multilayer stack deposited on ITO glass, see Scheme 1. Similar to the previous study of PtOEP-doped devices,[12,13] significant residual AlQ_3 emission could be observed at low doping concentrations (<3%). Higher platinum porphyrin concentrations (>10%) resulted in a significant drop in quantum efficiency due to self-quenching of the dye. Thus, 6% dye concentration was shown to provide the most saturated color and higher quantum efficiency.

The current−voltage ($I-V$) profiles in air at room temperature are shown in Figure 2. The turn-on voltages (V_T, defined as the voltage at which the power law dependence of I on V undergoes an abrupt change) for PtOX- and PtDPP-doped devices are 3.3 and 4.5 V, respectively. Bright red emission visible to the naked eye was observable at $V \geq V_T$. The brightness as a function of current density is plotted in Figure 3. In the low current density regime (0.1−10 mA/cm^2), the luminance of both devices shows a linear increase with current. In this regime the devices are also the most efficient (Figure 3). For the PtOX device, QE is 1.5% at 3.2 mA/cm^2, corresponding to a luminance of 23 cd/m^2 and a luminous efficiency of 0.3 lm/W. At 100 cd/m^2, the QE drops to 1.1% with a luminous efficiency of 0.17

---

(25) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Press: San Francisco, CA, 1978; p 170.
(26) Shelnutt, J. A.; Ortiz, V. *J. Phys. Chem.* **1985**, *89*, 4733.

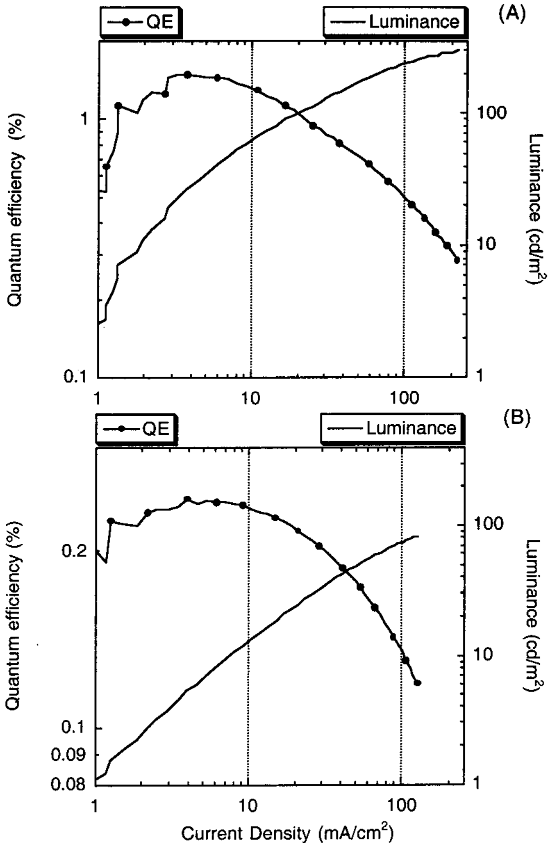


Figure 3. Quantum efficiency and luminance vs current density of the PtOX (A) and PtDPP (B) OLEDs.

lm/W which is comparable to the PtOEP device at the same molar concentration of doping which showed QE of 1.3% at 100 cd/m^2 with a luminous efficiency of 0.15 lm/W.[11] For the PtDPP device, the QE reaches a maximum of 0.25% at 3.9 mA/cm^2 with a luminance of 7 cd/m^2 and a luminous efficiency of 0.05 lm/W. At 100 cd/m^2, the QE = 0.12% with a luminous efficiency of 0.02 lm/W. The relatively poor performance of PtDPP compared to PtOX or PtOEP is primarily due to lower photoluminescence yield of PtDPP.

The electroluminescent (EL) spectra of the PtOX and PtDPP devices are shown in Figure 4. At low voltages (or current densities), the emission is from the platinum(II) porphyrin, resulting in sharp emission peaks at λ = 650 and 640 nm for PtOX and PtDPP, respectively. The EL spectra are very similar to their corresponding photoluminescence spectra, shown in Figure 1. No emission from the AlQ_3 host is observed, indicating complete energy transfer from the host exciton to the platinum porphyrin. The quality of emission spectra with regard to color and saturation are typically defined by their CIE chromaticity coordinates *x,y* (CIE = Commission Internationale de L'Eclairage).,[2,27,28] Acceptable red emitters have $0.55 \le x \le 0.74$ and $0.25 \le y \le 0.35$. CIE coordinates for devices held at a current density of 2 mA/cm^2 are (0.69, 0.30) and (0.67, 0.31) for PtOX and PtDPP, respectively, as shown in the chromaticity chart in Figure 5. The coordinates remain fairly unchanged up to current densities of 10 mA/cm^2.

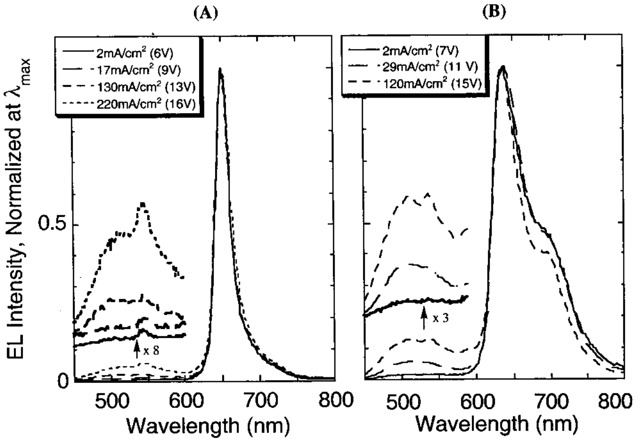


Figure 4. Electroluminescent spectra of the PtOX (A) and PtDPP (B) devices at different current densities and the corresponding driving voltages. The gradually increasing AlQ_3 emission region of 450−600 nm has been blown up and offset for clarity. Also note the appearance of the sharp line at 550 nm is due to platinum porphyrin singlet emission.

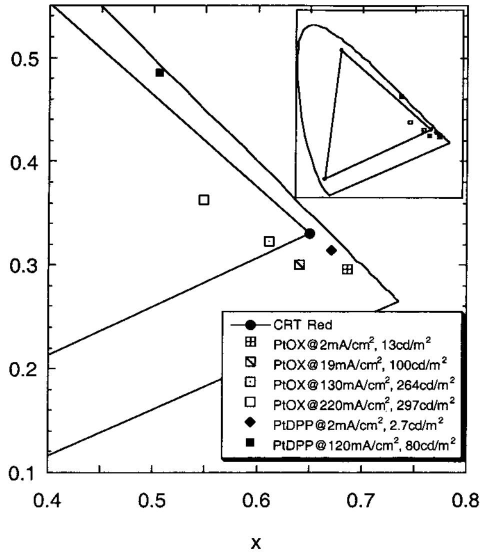


Figure 5. CIE coordinates and the corresponding brightness of the emission from the PtOX and PtDPP devices at low and high current regimes. The inset is the full CIE diagram and the RGB coordinates of a standard cathode ray tube display (CRT).

At higher current densities (>10 mA/cm^2), the luminances of both the PtOX and PtDPP devices increase sublinearly, resulting in a concomitant gradual decrease in QE (Figure 3). The emission color also changes from saturated red to orange due to increased emission between 450 and 610 nm. The EL spectra clearly indicate the emergence of peaks other than the porphyrin emission. These phenomena, occurring at high current densities, were also observed in PtOEP devices.[11−13] There are several factors contributing to the current dependence of the EL spectra. The first involves saturation of the emissive PtOX sites. There is a large difference between the singlet lifetime of AlQ_3 (10 ns)[29] and phosphorescence lifetime of the platinum porphyrins in AlQ_3 (39 and 21 μs for PtOX and PtDPP, respectively). The phosphorescent emissive sites near the HTL/ETL interface become saturated at medium to high current, i.e., most of the platinum porphyrins are promoted to their triplet excited state, which have a very

---

(27) Dartnall, H. J. A.; Bowmaker, J. K.; Mollon, J. D. *Proc. R. Soc. Lon. B* **1983**, *220*, 115.

(28) Gupta, B. D.; Goyal, I. C. *J. Photochem.* **1985**, *30*, 173.

long lifetime relative to the rate of formation of excitons near this interface. Once the platinum porphyrin dopants are saturated, AlQ_3 emission increases since there are no platinum porphyrin molecules in their ground state close enough to effectively transfer energy from the AlQ_3 singlet excitons prior to their relaxation (Figure 4). Increasing the platinum porphyrin doping level can eliminate the likelihood of saturation of phosphorescent sites. The residual emission from AlQ_3 can be suppressed in such a way, however, the trade off is the sacrifice of device efficiency due to self-quenching at high platinum porphyrin concentration.

It should be noted that the emission from AlQ_3, although weak compared to the major peak in the red, has a dramatic effect on the CIE coordinates. Since the coordinates are based on the human eye response, any emission near the peak in the photopic response function ($\lambda_{max} = 555$ nm) will have a more pronounced effect on the perceived color of the light source than emission significantly to the blue or red side of the peak. For example, for the PtOX device at 6 V and at 16 V (2 and 220 mA/cm^2, respectively), the spectra only differ by the comparatively weak emission between $\lambda = 450$ nm and $\lambda = 610$ nm seen in the EL spectrum at 16 V. The addition of this weak band leads to a pronounced shift in the CIE coordinates from (0.69, 0.30) at 6 V to (0.55, 0.36) at 16 V. Figure 5 shows the CIE coordinates of the electroluminescence at the low, medium, and high current density regimes. The OLED at 6 V appears pure red, while the device at 16 V appears orange to orange-red.

A second factor that contributes to the color change at high current densities is triplet−triplet annihilation ($T_1 + T_1 \rightarrow S_1 + S_0$)[25] taking place at high currents. The appearance and growth of the emission line centered at 550 nm in the electroluminescent spectra as the driving voltage increases (Figure 4) is indicative of this triplet quenching process. This peak does not match the well-studied emission of AlQ_3, but instead coincides with the weak singlet emission (i.e., fluorescence) of platinum porphyrins.[18] This 550-nm emission contributes to the shift of the perceived color of the OLEDs to the orange, as described above for the AlQ_3 contribution. Since triplet−triplet annihilation is a second-order process, the amount of triplet quenching and the resulting PtOX fluorescence are expected to increase significantly as the current is increased. PtOX fluorescence does not come from incomplete intersystem crossing (ISC) from the PtOX singlet to the PtOX triplet. If incomplete ISC were responsible for the 550-nm band, the ratio of the PtOX fluorescence to AlQ_3 emission should decrease as the amount of AlQ_3 fluorescence increases, since the ratio of AlQ_3 to total PtOX luminescence is increasing. The PtOX singlet signal increases relative to AlQ_3, however, consistent with their origin being from triplet−triplet annihilation.

Further evidence for triplet−triplet annihilation is seen in the small increase in brightness of the PtOX OLED as the current level was raised from 130 mA/cm^2 (red device) to 220 mA/cm^2 (orange device). That is, as the current was increased by 70%, the brightness only increases by 13%. If the color shift on increasing current were due only to saturation of the PtOX molecules, the contribution from PtOX to the emission intensity would be fairly constant and the AlQ_3 emission would grow in. The fluorescence from AlQ_3 is in the green to yellow part of the spectrum, where the contribution to the luminance on a per-photon basis is roughly 5 times greater than for red photons. This would lead to significantly enhanced luminescence, not a smaller than expected increase. If the contribution of AlQ_3 and PtOX fluorescence (450−600 nm) is subtracted from the spectra at 130 and 220 mA/cm^2, the luminance levels drop to 168 and 115 cd/m^2, respectively, corresponding to 64% and 39% of the total measured luminance values, respectively. Note that even though the current has been increased by a factor of 1.7 the amount light coming out of the device from PtOX phosphorescence has decreased by one-third. The fractional contribution of PtOX phosphorescence to the measured luminance decreased substantially as the current level is increased, consistent with enhanced triplet−triplet annihilation at the higher current level. A similar drop is observed in the quantum efficiencies estimated for red light only. If the contribution of the green/yellow part of the EL spectra are removed the quantum efficiencies at 130 and 220 mA/cm^2 drop to 0.39% and 0.24%, respectively.

The PtDPP OLED is not as efficient as the PtOX device, and the contribution to the emission from AlQ_3 has a stronger effect on the loss of the red color saturation for PtDPP-based OLEDs. At 130 mA/cm^2, the PtDPP device has become yellow, consistent with a greater AlQ_3 emission mixed with the PtDPP emission.

In conclusion, we have demonstrated the use of two new platinum porphyrins as efficient red phosphorescent dyes in small molecule-based OLEDs. Both dyes, at 6% doping level into AlQ_3, give saturated red emission at drive voltages < 10 V. Higher current densities lead to saturation of phosphorescent emissive sites. Triplet−triplet annihilation, producing platinum porphyrin singlet excitons, was also observed at high current. PtOX-doped devices reach a quantum efficiency of 1.1% at 100 cd/m^2 with a luminous efficiency of 0.17 lm/W.

Acknowledgment. We thank Universal Display Corporation, the Defense Advanced Research Projects Agency, and the National Science Foundation for financial support of this work. The authors also thank Mr. Sergey Lemansky for his assistance with the lifetime measurements. S. Sibley thanks support of the Camille and Henry Dreyfus Foundation and the Beatrice Aitchison ‘28 fund of Goucher.

CM9906248

---

(29) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F. *Inorg. Chem.* **1986**, *25*, 3858.