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Highly efficient electrophosphorescent polymer light-emitting devices

Tzung-Fang Guo [a], Shun-Chi Chang [a], Yang Yang [a,*], Raymond C. Kwong [b], Mark E. Thompson [b]

[a] *Department of Materials Science and Engineering, University of California at Los Angeles, Los Angeles, CA 90095, USA*
[b] *Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA*

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Abstract

We report a high performance polymer electroluminescent device based on a bi-layer structure consisting of a hole transporting layer (poly(vinylcarbazole)) and an electron transporting layer poly(9,9-bis(octyl)-fluorene-2,7-diyl) (BOc-PF) doped with platinum(II)-2,8,12,17-tetraethyl-3,7,13,18-tetramethylporphyrin (PtOX). The devices show red electrophosphorescence with a peak emission at 656 nm and a full width at half maximum of 18 nm, consistent with exclusive emission from the PtOX dopants. BOc-PF emission is not observed at any bias. The required doping levels for these phosphorescence-based polymer light-emitting diodes (PLEDs) are significantly lower than for other reported phosphorescence-based PLEDs or organic light-emitting diodes (OLEDs). A doping level of 1% or more give an LED with exclusive PtOX emission, whereas related PLEDs or OLEDs doped with phosphorescent dopants require doping levels of >5% to achieve exclusive dye dopant emission. The device external efficiency was enhanced from 1% to 2.3% when doped with PtOX. The lower doping level in BOc-PF/PtOX based PLEDs decreases triplet–triplet annihilation in these devices, leading to quantum efficiency that is only weakly dependent on current density. The luminescence transient decay time for this device is ~500 μs.

Since the first successful demonstration of polymer light emitting diodes (PLEDs) from a conjugated polymer in 1990, PLEDs have attracted worldwide attention as a candidate for the next generation of emissive flat panel displays. However, there are several disadvantages associated with conjugated polymers as the active materials for the emissive display. The emission spectra from conjugated polymers are often too broad for the application as a full color display, since the resulting emission is typically not saturated. Moreover, the majority of PLEDs reported to date emits from a fluorescent transition, severely limiting the quantum efficiency. The quantum efficiency of a device emitting from a fluorescent material is limited by the low theoretical ratio of singlet excitons (25%) compared to triplet excitons (75%) which are formed upon electron–hole recombination in the electroluminescent process [1,2]. Experimental results confirm this low singlet to triplet exciton ratio [3]. Recently, highly efficient organic light emitting diodes (OLEDs) doped with phosphorescent dyes have been demonstrated [4–7]. By employing phosphorescent dyes in which

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[*] Corresponding author.
E-mail address: yangy@ucla.edu (Y. Yang).

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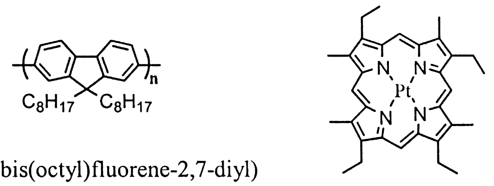
both the singlet and the triplet states participate the emission process, highly efficient red and green OLEDs have been achieved. By doping a platinum (II) porphyrin into aluminum (III) tris(8-hydroxyquinolate) (Alq_3), saturated red emission can be achieved with Commission International de L'Eclairage (CIE) chromaticity coordinates at (0.69, 0.30) [7]. Two different platinum porphyrin complexes have been used to fabricate red phosphorescent OLEDs, i.e. platinum (II) 2,8,12,17-tetraethyl-3,7,13,18-tetramethylporphyrin (PtOX) and platinum octaethylporphyin (PtOEP). OLEDs made with the two phosphors give nearly identical spectra and device characteristics [7]. By choosing an iridium complex, $Ir(ppy)_3$ as the green electrophosphorescent dopant, a peak quantum efficiency greater than 8% has been achieved with CIE chromaticity coordinates at (0.27, 0.63) [6].

The use of phosphorescent dopants has been applied to PLEDs. However, to our knowledge, PLEDs using phosphorescent dyes as the dopant have not reached the high quantum efficiencies reported for the phosphorescence based OLEDs [8,9]. The cause of the low quantum efficiency for those PLEDs is not known, however, it may be to incompatibility of the dopant with the polymer system. In this paper, we demonstrate a PLED employing poly(9,9-bis(octyl)-fluorene-2,7-diyl) (BOc-PF) as the host material doped with PtOX. The chemical structures of PtOX and BOc-PF are shown in Scheme 1. These BOc-PF/PtOX based PLEDs give good external quantum efficiencies, comparable to recently reported small molecule based OLEDs using the same dopant but at a much higher concentration [5].



poly(9,9-bis(octyl)fluorene-2,7-diyl)

PtOX

Scheme 1.

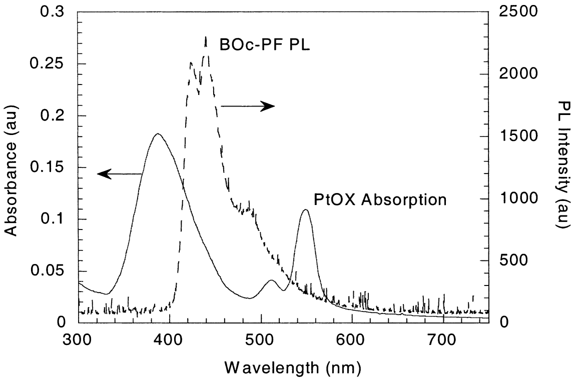


Fig. 1. The emission spectrum of BOc-PF and PtOX.

In order to get dominant emission from a dopant in an organic thin film the excitons formed by hole–electron recombination in the matrix must efficiently be transferred to the dopant. Both dipole–dipole (Förster) and electron-exchange (Dexter) energy transfer process require good overlap between the host emission spectrum and the dopant's absorption spectrum to be efficient [11]. Fig. 1 shows the absorption and photoluminescence (PL) spectra of PtOX and BOc-PF. This system shows a good spectral overlap between the emission spectrum of BOc-PF and the Soret band ($\lambda_{max} = 385$ nm) and Q-bands ($\lambda = 500$–575 nm) of PtOX, suggesting that energy transfer from BOc-PF to PtOX will be efficient. Comparable spectral overlap has not been reported for other Pt porphyrin doped PLEDs [8]. The efficiency of energy transfer from the host matrix to the dopant can be examined by looking at the PL spectra of films with a range of dopant concentrations. An efficeint system will not require high dopant concentration to give only dopant-based emission. The energy transfer mechanism can involve either a Förster or Dexter process, but the Förster transfer process is expected to dominate, since photoexcitation gives only singlet excitons. For these PL measurements, thin films of BOc-PF containing 0.1%, 1% and 5% of PtOX were prepared. The corresponding PL spectra are shown in Fig. 2. At a concentration of 0.1% PtOX, the energy transfer was not complete, and the main PL was from BOc-PF. At a 1% doping level, the energy transfer from BOc-PF to PtOX was nearly complete. Residual BOc-PF emission was observed on increasing the PtOX

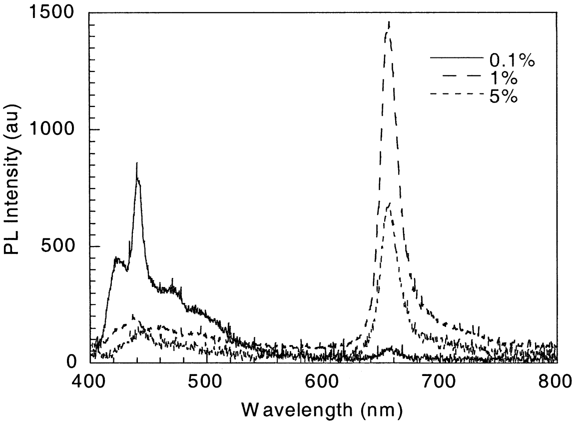


Fig. 2. The PL emission spectra of BOc-PF films doped with 0.1%, 1% and 5% of PtOX.

percentage further to 5%. This weak BOc-PF emission was probably due to the fast fluorescent transition within BOc-PF, and/or phase separation between the BOc-PF and PtOX. When the doping concentration of PtOX exceeded 1%, self-quenching was observed, which is evident in the lower PL efficiencies for samples doped with 5% PtOX, as shown in Fig. 2. The fact that nearly complete quenching of BOc-PF emission is observed at a 1% doping level shows that energy transfer from BOc-PF to PtOX is also a very efficient process. It should be stressed, however, that PL measurements do not address the efficiency of triplet exciton transfer from BOc-PF to PtOX. The energy of the BOc-PF triplet is not known, so we cannot a priori estimate the efficiency of the triplet energy transfer process. Assuming a normal Stokes shift between the singlet and triplet energy levels [12] we expect the BOc-PF triplet levels to line up reasonably well with the PtOX Q-bands leading to good Dexter energy transfer from BOc-PF to PtOX.

O'Brien et al. reported that the PL efficiency of PtOEP is higher in 4,4′-dicarbazoyl-biphenyl (CBP) than that in Alq_3 [5]. Their conclusion was based on the longer luminescent lifetime of PtOEP doped in CBP (>90 μs) compared to PtOEP in Alq_3 (35 μs), indicative of more efficient *non*radiative relaxation in Alq_3. Emission from the CBP exciton is blue, while the Alq_3 exciton emits green light. The energetic overlap of the excitonic states of PtOEP overlap much more strongly with Alq_3 than with CBP. The comparatively lower energetic overlap of the PtOEP and CBP excitons leads to a lower probability for exciplex formation and reverse energy transfer from PtOEP to the CBP host matrix than for the Alq_3 matrix. Since both exciplex formation and reverse energy transfer lead to nonradiative quenching of the PtOEP exciton, one would expect a higher luminance quantum efficiency for PtOEP in CBP, as observed. Thus, we expect that the highest electrophosphorescent efficiency can be achieved by employing an efficient blue host polymer doped with platinum porphyrins such as BOc-PF. The measured luminescent lifetime of PtOX doped at 1% in BOc-PF is 55 μs, indicative of efficient luminescence from PtOX. Thus BOc-PF is an ideal candidate as the host polymer for highly efficient PLEDs with emission from electrophosphorescent PtOX.

The PLEDs studied here were bilayer devices consisting of a hole transporting layer of poly(vinylcarbazole) (PVK) and an electron transporting luminescent layer of BOc-PF, doped with PtOX. Indium tin oxide (ITO) coated with a thin layer of conducting polymer (PEDOT 3,4-polyethylenedioxythiophene-polystyrenesulfonate) as a bilayer electrode was used as an anode [10]. A PVK layer was formed by spin-casting from a 1,2-dichlorobenzene solution at 4000 rpm (ca. 200 Å). A layer of BOc-PF doped with PtOX was deposited on top of the PVK layer by spin-casting a toluene solution of BOc-PF/PtOX (ca. 1200 Å) on the preformed and dried PVK film. This method did not perturb the recoated PVK film. Thermal evaporation of a calcium cathode (500 Å) was carried out at a pressure of roughly 1×10^{-6} Torr followed by an overcoating of a 1000 Å thick aluminum layer. The device area for these PLEDs was 0.1 cm^2.

Although the PL spectra in Fig. 2 shows minor contributions from BOc-PF when it is doped with 1% of PtOX, the electroluminescene (EL) spectra show exclusive emission from PtOX, Fig. 3. A doping level of 1% is close to the values typically used for fluorescence based OLEDs and PLEDs [11]. Typically, phosphorescencebased OLEDs and PLEDs must be doped at higher concentrations (>5%) in order to get complete energy transfer at all bias levels. The ability to dope BOc-PF based

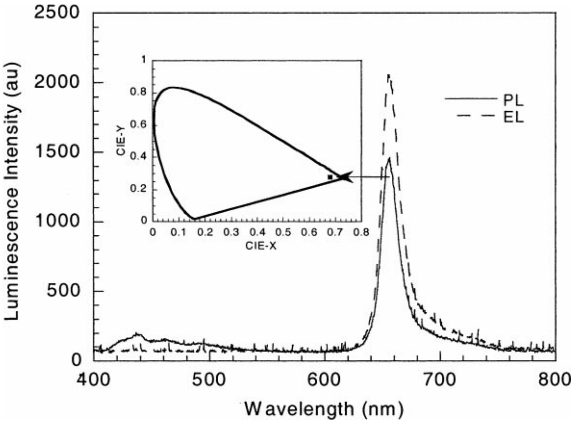


Fig. 3. The PL and EL spectra for BOc-PF PLED doped with 1% PtOX. The inset shows the CIE chart of the corresponding EL emission.

PLEDs at low levels may be an indication that the exciton diffusion length is very long in this polymer, preventing dye saturation and resultant host emission at low doping levels or high current densities [3,7]. The EL spectra obtained from BOc-PF doped with 1% PtOX is centered at 656 nm with a small full width half maximum (FWHM) of ~18 nm. The shapes of the EL emission spectra and CIE coordinates (0.68, 0.28) of PLEDs from BOc-PF doped with PtOX (inset of Fig. 3) are independent of the device bias. This is in contrast to what has been observed in OLEDs utilizing Alq_3 doped with PtOX as the active medium [7], which can show host emission in addition to PtOX or PtOEP at higher bias levels.

Comparison of the EL spectra of the 1% PtOX doped PLED and the PL spectrum of a film of the same composition (Fig. 3) shows that energy transfer to PtOX is more efficient in EL than in PL. Weak BOc-PF emission is observed in the PL spectrum, while only PtOX emission is observed in the EL spectrum. The reason that the two spectra are different is related to the mechanisms used to generate excitons at the PtOX dopants in the PL and EL processes. In the PL experiment, only energy transfer processes (either Förster or Dexter) from BOc-PF to PtOX can give PtOX based excitons. These energy transfer processes do not show complete transfer even at a 5% doping level (Fig. 2). In the PLED, however, both energy transfer and carrier trapping can lead to exciton formation at the PtOX dopant. The LUMO level of PtOX is expected to be below that of BOc-PF, making the dopant a reasonable electron trap in this doped film [7]. Hole–electron recombination at the PtOX dopant will lead to exciton formation at the dopant, without direct energy transfer from BOc-PF. The injection current continues to decrease for LEDs with higher doping concentrations; however, the device turn-on voltage, which is determined by the injection of minority carriers, remains more or less unchanged for different doping concentrations that we tested. This is a clear evidence that the PtOX is an efficient trap for electrons, which is the majority carrier for polyfluorene polymer. Subsequently, the trapped electrons at the PtOX sites behave as the traps for the in-coming holes, hence the exciton formation is enhanced. (This is so-called “the sequential carrier trapping process”.)

PLEDs with doping levels of 0.1% and 5% PtOX were also tested, and they gave lower efficiencies than observed for the 1% doped PLED. Two layer PLEDs prepared with undoped BOc-PF give blue EL emission, with an external quantum efficiency of 1%. When 1% of PtOX is added to the BOc-PF, the device peak quantum efficiency increased by 2.3% at 11 cd/m^2. Fig. 4 illustrates a typical current–light–voltage (*I–L–V*) characteris-

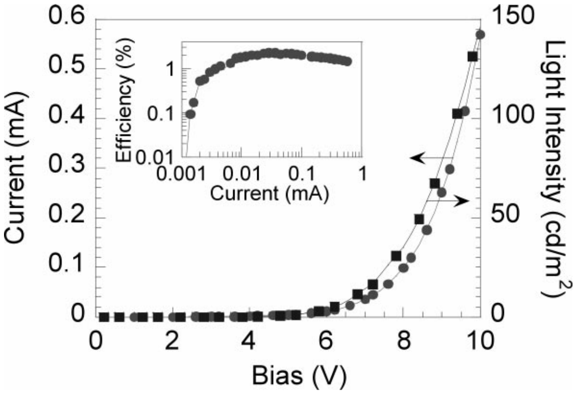


Fig. 4. The *I–L–V* curves of the PLED. The inset shows the quantum efficiency at different injection current intensities. The device area is about 0.1 cm^2.

tic of the PLEDs used in this study. This device turns on at 3.7 V and reaches a brightness of 100 cd/m^2 at close to 9 V. To our knowledge, this is significantly higher than any other reported quantum efficiency for a PLED doped with a phosphorescent dye.

An important characteristic of our phosphorescence based polymer LED is that the device quantum efficiency remains at a relatively high value even at high device brightnesses, see the inset to Fig. 4. For example, our PLED has a 1.6% quantum efficiency at 100 cd/m^2, this is a significant improvement over the previously reported polymer LEDs [9]. OLEDs prepared with PtOEP or PtOX dopants show a significant decrease in quantum efficiency as the current density is increased [3–7]. This decrease has been attributed to luminescence quenching by triplet–triplet annihilation (TTA), which becomes progressively more severe as the current density is increased [5,7,13–16]. Pt porphyrin based OLEDs were typically doped at the 4–6% level. By lowering the doping level to 1% in the PLEDs reported here, the average dopant–dopant distance has been increased, leading to a significant decease in TTA and a fairly constant efficiency as a function of current density. If the Pt porphyrin doping level in Alq_3 or CBP based OLEDs is decreased to 1%, TTA is decreased, however, substantial host emission is observed at the lower doping level [3,5,7,13].

One of the concerns in using phosphorescent dopants in PLEDs is the response time. For display applications, it is required to have a sufficiently fast response time, usually in the millisecond range or shorter. Fig. 5 shows the transient response of the electrophoresence from our devices. Pulsed voltage was applied to the device and the optical signal was sent to an oscilloscope. As shown in Fig. 5, a decay time of 0.5 ms was observed, which is sufficiently small for most display applications. This 0.5 ms decay time is consistent with a phosphorescent emission process. Curiously, the half-life of this decay is 150–200 μs, which is significantly longer than the lifetime obtained from the PL measurement on an identical film of BOc-PF/PtOX (~55 μs). We are currently investigating the origin of this difference.

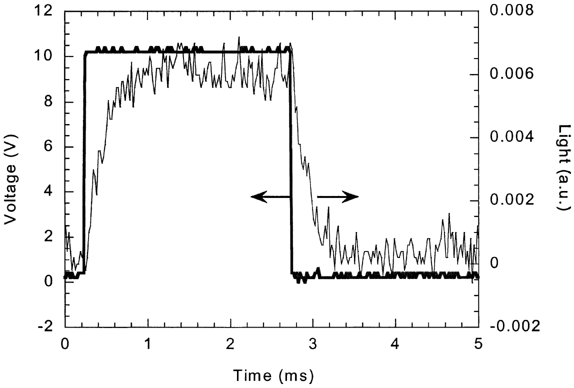


Fig. 5. The transient response of the BOc-PF PLED doped with 1% of PtOX. The device response time is about 500 μs.

In conclusion, we have demonstrated the use of a platinum (II) porphyrin as an efficient red electrophosphorescent dopant in polyfluorene polymer based PLEDs. Excellent device performance is achieved. Saturated red emissive light is obtained, and a 2.3% peak quantum efficiency is achieved at a 1% PtOX doping level. This comparatively low doping level decreases TTA quenching, leading to a quantum efficiency that is only weakly dependent on current density. To our best knowledge, this is by far the best performance polymer LED doped with phosphorescent emitters. Our data suggests that the phosphorescent dopant creates a new direction for achieving high performance PLEDs and displays.

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