



New charge-carrier blocking materials for high efficiency OLEDs

Vadim I. Adamovich^a, Steven R. Cordero^a, Peter I. Djurovich^a,
Arnold Tamayo^a, Mark E. Thompson^{a,*}, Brian W. D'Andrade^b,
Stephen R. Forrest^b

^a Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA

^b Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering and the Princeton Materials Institute, Princeton University, Princeton, NJ 08544, USA

Abstract

Three strategies for preparing high efficiency OLEDs are demonstrated, which involve the use of hole and electron blocking layers. The first of these strategies involves the use of a cyclometallated iridium compound (bis(2-(4,6-difluorophenyl)pyridyl-*N,C2'*)iridium(III) picolinate, FIrpic) as a hole-blocking material for green and blue emissive OLEDs. Devices which utilized FIrpic as a combined hole blocking and electron transporting layer gave external quantum efficiencies > 14% (device structure: anode/HTL/EL/FIrpic/cathode, HTL = hole transport layer, EL = emissive layer). When the FIrpic layer of this device was replaced with bathocuproine (BCP), the device efficiency dropped to 12%. A host-guest approach to the formation of a hole blocking layer (HBL) has also been demonstrated. FIrpic was doped into two different wide energy band-gap organic matrix materials (i.e. octaphenyl-cyclooctatetraene, OPCOT, and 1,3,5-tris-phenyl-2-(4-biphenyl)benzene, SC5) forming a mixed HBL. Devices with doped OPCOT gave quantum efficiencies comparable to those with a BCP HBL, while the SC5 based devices gave higher efficiency than their BCP blocked counterparts. When blue electrophosphorescent devices are prepared in a conventional OLED structure (i.e. anode/HTL/EL/HBL/ETL/cathode), excessive HTL emission is often observed, resulting from electron leakage from the doped CBP layer into the HTL. This electron leakage can be eliminated by inserting an electron blocking layer (EBL) between the HTL and luminescent layers. Both fac-tris(1-phenylpyrazolato-*N,C2'*)iridium(III) (Irppz) and Iridium(III) bis(1-phenylpyrazolato-*N,C2'*)(2,2,6,6-tetramethyl-3,5-heptanedionato-*O,O*) have been used as efficient EBLs. The insertion of an EBL leads to both improved color purity and quantum efficiency, relative to devices without EBLs. For example, a white emitting device with the structure ITO/HTL/EL/HBL/ETL/LiF/Al gave an external efficiency of 1.9% and nearly exclusively HTL emission. Addition of a 100 Å Irppz layer between the HTL and EL gave a device with an external quantum efficiency of 3.3% and electroluminescence from only the EL.

© 2003 Elsevier B.V. All rights reserved.

1. Introduction

Considerable progress has been made in enhancing the efficiencies of organic light emitting diodes (OLEDs). The first breakthrough came

* Corresponding author.

E-mail address: met@usc.edu (M.E. Thompson).

with the report of efficient electroluminescence from an organic thin film heterostructure [1]. This device consisted of two organic layers, a hole transporting tri-arylamine and an electron transporting aluminum coordination complex. Emission in this device came from the metal complex layer, i.e. aluminum-tris(8-hydroxyquinolate), Alq₃. Shortly after that report, it was demonstrated that significant efficiency enhancements could be achieved by adding fluorescent dopants to the light emissive layer [2]. The dopant is present in low concentration, trapping excitons and preventing self-quenching in the luminescent layer. The doped device is typically a double heterostructure rather than the single heterostructure used for undoped OLEDs. This double heterostructure consists of separate hole transporting (HTL), emissive (EL) and electron transporting (ETL) layers, leading to efficient hole-electron recombination in the luminescent layer. This dopant approach led to efficiencies close the theoretical limits for a fluorescence based device (25% internal quantum efficiency, ≈5% external) [3]. The next significant step in increasing device efficiencies involved the incorporation of a phosphorescent dopant into the structure [4]. The phosphorescent dopant allows the device to efficiently utilize both singlet and triplet excitons, leading to reported efficiencies close the absolute theoretical limit of 100% (internal efficiency) [3].

While phosphorescent dopants can lead to significantly enhanced quantum efficiencies, they also have required more complex device architectures. Singlet excitons have short diffusion lengths, on the order of tens to hundreds of Angstroms. Triplet states have much longer lifetimes than their singlet counterparts, allowing them to diffuse >1000 Å [4,5]. Thus, it is essential to use device structures that physically confine the excitons within the luminescent layer. Triplet exciton confinement in a three layer double heterostructure is possible if the HTL and ETL have higher optical energy gaps than the exciton binding energy, but this is not always achieved with common OLED materials. A good example is seen in devices with the red phosphorescent emitter, PtOEP, doped into a CBP (4,4'-N,N'-dicarbazolebiphenyl) host [5]. A single heterostructure device was prepared (ITO/NPD/

CBP-PtOEP/Alq₃/Mg–Ag) and gave an external efficiency of 4.2%. PtOEP has a triplet energy of 1.9 eV, and those of NPD and Alq₃ are 2.3 and 2.0 eV, respectively [6]. It is energetically unfavorable, therefore, for excitons from the CBP layer to diffuse into the adjacent NPD HTL, but the Alq₃ triplet energy is close to that of PtOEP and hence does not act as a good barrier to exciton diffusion out of the EL. O'Brien et al. demonstrated a simple solution to the problem of exciton leakage, by inserting an exciton blocking layer between the doped CBP and the Alq₃ electron transporting layers (i.e. ITO/NPD/CBP–PtOEP/BCP/Alq₃/Mg–Ag, BCP = bathocuproine) [5]. BCP has a triplet energy of 2.5 eV, significantly higher than that of PtOEP. The BCP layer effectively blocks the diffusion of PtOEP excitons into the Alq₃, where they would have nonradiatively recombined. An added benefit of the BCP layer is its deep HOMO level (6.5 eV), which efficiently blocks the diffusion of holes from the luminescent layer into the Alq₃ layer. Thus, the BCP forms a combined hole/exciton blocking layer. The result is a marked improvement in the device efficiency, from an external efficiency of 4.2% for the device without hole-blocking to 5.6% with BCP [5]. The effect of the BCP blocking layer can also be seen in the electroluminescence spectra. The unblocked device has a significant Alq₃ contribution to the EL spectrum, resulting from hole leakage into the Alq₃ layer, while the BCP blocked device gives a spectrum consistent with only PtOEP emission.

The need for efficient exciton and hole-blocking layers is also seen in Ir phosphor based OLEDs. Baldo et al., reported efficient green emission from Irppy (*fac* tris(2-phenylpyridine) iridium) doped in CBP [7]. The device structure was ITO/NPD/CBP–Irppy/BCP/Alq₃/Mg–Ag, and gave a peak quantum efficiency of 9%. If the BCP layer was omitted, the efficiency dropped dramatically, to only 0.2%. The BCP layer blocks excitons, and also prevents holes from migrating from the doped CBP layer into the ETL. The HOMO energies for Irppy, BCP and Alq₃ (5.3, 6.5 and 5.7 eV, respectively) are consistent with the observed blocking, i.e. there is a 1.2 eV hole barrier between the Irppy and BCP HOMOs. The hole-blocking function is not as

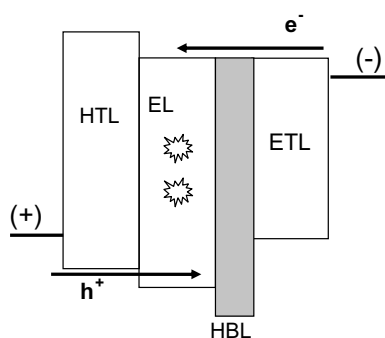


Fig. 1. Schematic energy level diagram of high efficiency electrophosphorescent OLED. Holes transport along HOMO energy levels, electrons—along the LUMO levels. Excitons are indicated as starburst patterns.

important for PtEOP, since its HOMO level is well above that of Alq₃.

The role of a hole/exciton blocker can be seen in the energy level diagram of Fig. 1. For a materials to be an efficient hole-blocker, it must have a HOMO level deeper than that of the dopant or host material, and the triplet energy of the blocking material must be high enough to efficiently prevent the migration of triplet excitons out of the luminescent layer. The two most common hole-blocking materials are BCP [7–10] and BAQ (4-biphenyloxolato aluminum(III)bis(2-methyl-8-quinolinato)4-phenylphenolate) [11–13]. A number of other organic materials have also been used as hole-blocking materials, e.g. fluorinated phenylenes [14], oxidazole and triazol containing molecules TPBi, PBD, TAZ [15,16], 1,8-naphthalimides [17], polyquinolines [18] and carbon nanotubes doped into PPV [19].

While a number of hole-blocking materials have been investigated in the past, the need for an electron blocking in electrophosphorescent devices has only recently become apparent with the demonstration of blue and white electrophosphorescence [20]. For example, blue electrophosphorescent devices can show significant NPD emission in their spectra, resulting from electron leakage into the HTL. The present paper consists of two parts. The first discusses the use of Ir complexes as hole-blocking materials. The electron blocking layer (EBL) concept, and some examples of metal

complexes used as electron-blockers, are discussed in the second part of the paper.

2. Experimental

Pre-patterned 2 mm wide striped anodes of indium tin oxide (ITO) predeposited on glass substrates (with a sheet resistance of 20 Ω/□) were cleaned by sonication in a detergent solution, then rinsed with deionized water, followed by boiling in trichloroethylene, acetone and ethanol for 3–4 min in each solvent. After cleaning, the substrates were dried under N₂ followed by exposure to UV and ozone for 10 min.

Organic layers were sequentially deposited at a rate of 2.5 Å/s onto room temperature substrates by thermal evaporation from resistively heated tantalum boats in vacuum, at a base pressure of ~3–4 × 10⁻⁶ Torr. The rate of single component layer deposition was monitored with a quartz crystal thickness monitor located close to the substrate. For two component emissive or hole-blocking layers, the evaporation rate of the dopant was controlled with an additional crystal monitor located near to the dopant evaporation source. The additional monitor was not exposed to the evaporating host, allowing for precise monitoring of the dopant flux.

After deposition of the organic films, the chamber was vented, and a shadow mask with 2 mm wide stripes was mounted transverse to the ITO rows. The cathode consisted of 10 Å thick LiF layer followed by a 1000–1500 Å thick layer of aluminum deposited at 0.3–0.4 Å/s for LiF, and 3–4 Å/s for AL. Alternatively, 1000 Å thick Mg:Ag (10:1) cathodes were co-deposited from separate sources at a rate 0.2 Å/s for Ag, and 2.0 Å/s for Mg, and subsequently capped with a 300–500 Å thick layer of Ag to prevent oxidation. The OLEDs were formed as 2 × 2 mm squares at the intersections of ITO anode and cathode stripes.

The devices were characterized in air within 2 h of fabrication. Current–voltage measurements were made with a Keithley Source Meter (model 2400). Light intensity was measured using a Newport model 1835 optical power meter and 818-UV Newport detector [21]. Electroluminescence

spectra were measured with a Photon Technology International fluorimeter.

3. Results and discussions

3.1. Hole-blocking materials

The choice of material for efficient hole-blocking is based on a number of parameters. The material must have a wide energy band-gap (singlet and triplet states),¹ a deep HOMO (i.e. a high ionization energy) and the LUMO should be closely aligned with that of the ETL. Furthermore, it should be readily sublimable, forming uniform amorphous films, since these OLEDs consist of several organic layers that can not be readily prepared by solution deposition methods.

The most commonly used materials for hole-blocking layers (HBLs) in electrophosphorescent LEDs, meeting all the requirements listed above, are BCP [8–11] and BAQ [11]. Both BCP and BAQ have high singlet energy gaps and appropriately placed HOMO and LUMO energies, but their triplet energies are below 2.4 eV. These low triplet energies limit their usefulness in blocking blue or green triplet excitons. In the search for higher energy phosphorescent dopants, we have prepared a number of materials with high energy triplet states. An example of a high energy phosphor is FIRpic (bis(2-(4,6-difluorophenyl)pyridyl-*N,C2'*)iridium(III) picolate, Fig. 2) [11]. This metal complex has a triplet energy of 2.6 eV, well above the green, yellow and red emissive dopants that have been used in phosphorescence based OLEDs. Complexes such as FIRpic are typically stable toward both oxidation and reduction, have a high glass transition temperature, T_g , and form glassy films [23,24]. Moreover, the HOMO and LUMO energies of the metal complexes can be

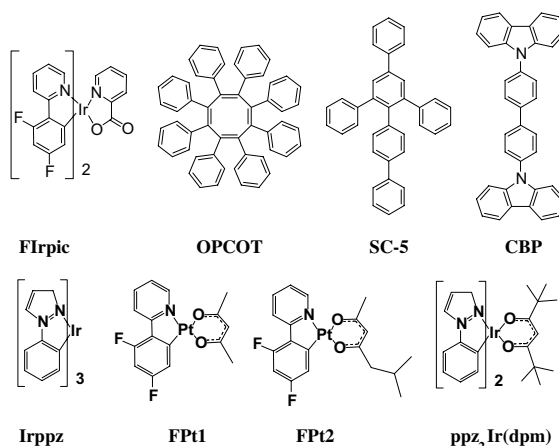


Fig. 2. Structures and acronyms for the compounds discussed.

readily tuned with suitable metal and ligand combinations [9]. The HOMO energy for FIRpic has been estimated by both electrochemical and ultraviolet photoelectron spectroscopic (UPS) measurements, and is at 5.8 eV (see Table 1: all energies are quoted with respect to the vacuum level). The LUMO energy is at ~ 2.7 eV, inferred from the HOMO energy and either its reduction potential or optical energy gap, placing it close to those of typical electron transporting materials and hosts (LUMO energies: Alq₃ = 3.0 eV, CBP (4,4'-*N,N'*-dicarbazolebiphenyl, see Fig. 3) = 2.8 eV). Thus, the high triplet energy and relative alignments of the FIRpic HOMO and LUMO levels make it suitable as an HBL.

The first device in which FIRpic was used as an HBL were green OLEDs, with a structure similar to the conventional double heterostructure used for the electrophosphorescent OLEDs (i.e. anode/HTL/doped EL/ETL/cathode). The emissive layer in these devices was a Irppy doped CBP film [9], with the following OLED structure: ITO/NPD(400 Å)/CBP:Irppy(8% 300 Å)/FIRpic (200 Å)/Alq₃(150 Å) /LiF/Al. The quantum efficiencies of OLEDs with a FIRpic HBL ($\eta_{\text{ext}} \sim 10\%$, Fig. 3) are very similar to those reported by Baldo et al. [7], for closely related devices with a BCP blocking layer in place of FIRpic. The LUMO energies of FIRpic and BCP are close to that of Alq₃, suggesting that both of these HBL materials are also efficient electron injection layers. Thus, a single

¹ Singlet energies are estimated from the overlap of the normalized absorption and emission spectra [22]. The triplet energy is estimated as the λ_{max} value for the highest energy feature in the phosphorescence spectrum. Heavy metal complexes give efficient phosphorescence at room temperature, while organic materials (e.g. CBP, NPD, etc.) must be cooled to 77 K or lower to observe phosphorescence [6].

Table 1
Estimated HOMO, LUMO and triplet exciton energy levels of selected OLED materials

Compound	HOMO/eV	LUMO/eV	T_1 energy/eV
NPD	5.5	2.4	2.3
CBP	6.1	2.8	2.6
SC5	6.2	2.6	2.5 ^a
OPCOT	6.1	2.8	^b
Firpic	5.8	2.9	2.7
BCP	6.5	3.2	2.5
FPt1	6.0	2.9	2.8
ppz ₂ Ir(dpm)	5.3 ^c	2.2	2.4
Irppz	5.1	1.7	3.1

Unless otherwise noted, the HOMO levels come from UPS measurements and the LUMO levels are estimated using the optical energy gap (singlet absorption). The triplet energy was estimated as the λ_{\max} of the phosphorescence spectrum, unless otherwise noted.

^a This value was estimated by Stern–Volmer quenching studies, see [28].

^b OPCOT did not phosphoresce at low temperature and had a solubility too low for the Stern–Volmer quenching method.

^c Value estimated by cyclic voltammetry.

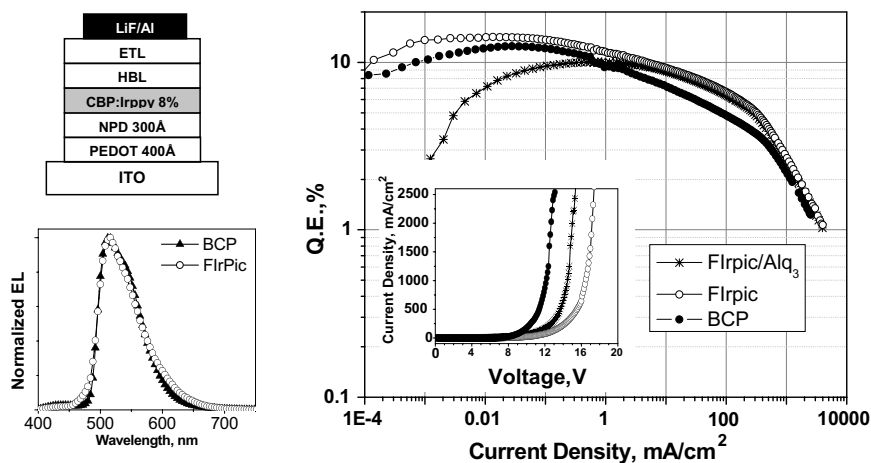


Fig. 3. The structure (upper left), EL spectra (lower left), and device performance plots (right) for green phosphorescent OLEDs with three different hole-blocking layers. The device structures are described in the text.

layer of either Firpic or BCP can be used to both block holes and transport electrons (HB·ETL). To investigate this, a second set of devices was prepared in which the 200 Å Firpic and 150 Å Alq₃ layers were replaced with a single Firpic or BCP layer (i.e. with structure ITO/PEDOT(300 Å)/NPD(300 Å)/CBP:Irppy(8% 300 Å)/HB·ETL (400 Å)/LiF/Al, HB·ETL = Firpic, BCP). The device structures, efficiencies, current–voltage characteristics, and spectra are shown in Fig. 3. The efficiencies of the simplified Firpic HB·ETL OLEDs are markedly higher than for devices with an Alq₃

ETL ($\eta_{\text{ext}} = 14.2\%$ versus 10.0% , respectively). The current–voltage characteristics are consistent with Firpic having a LUMO level above that of BCP, since the Firpic-based HB·ETL device requires a higher bias to achieve a given current. Higher quantum efficiencies were observed for OLEDs with a Firpic HB·ETL than for those with BCP (14.2% versus 12.1% , respectively). The higher efficiency for the Firpic-based device is most likely due to the high triplet energy for Firpic, making it a more effective exciton blocker than BCP (Table 1).

It is also possible to make blue emissive OLEDs with FIrpic as the hole blocking material. Blue OLEDs were prepared with CBP:FIrpic emitting layers and neat FIrpic as the HBL material (ITO/NPD(300 Å)/CBP:FIrpic 6%(300 Å)/FIrpic (200 Å)/Alq₃ (150 Å)/Mg:Ag/Ag). The EL spectra of these FIrpic blocked devices had the same emission maxima as BCP blocked devices ($\lambda_{\text{max}} = 470$ nm), however, they give broader spectra than those with a BCP HBL. The EL spectrum is similar to that of a thin film of pure FIrpic, Fig. 4(a). The spectral broadening is due a contribution from the neat FIrpic HBL. The emission spectrum for a neat thin film of FIrpic is broader than that

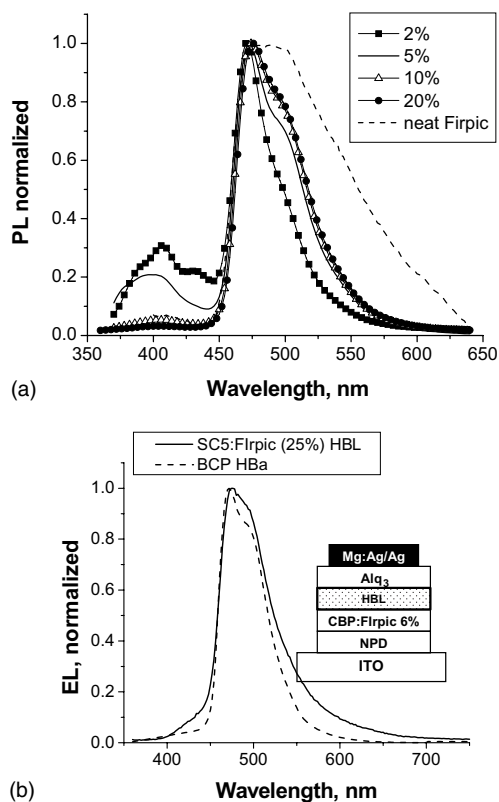


Fig. 4. (a) Photoluminescence spectra of CBP:FIrpic doped and neat FIrpic thin films. (b) Electroluminescence spectra and device structures for blue emissive OLEDs, with SC5:FIrpic and BCP hole-blocking layers. The device characteristics are given in Table 2. The device structure is: ITO/NPD(300 Å)/CBP:FIrpic(6%, 300 Å)/HBL(150 Å)/Alq₃(200 Å)/Mg:Ag(1000 Å).

of the doped FIrpic films (Fig. 4). The broadening in neat FIrpic is presumably due to solid state solvation effects (SSSE) in the amorphous thin film [25]. The quantum efficiency of the OLED with a FIrpic HBL was nearly identical to the efficiency of the same device with a BCP HBL. While FIrpic efficiently blocks holes and excitons from migrating out of Irppy-doped CBP layers, it is not effective at confining blue excitons, making it primarily useful as an HBL for green to red emitting OLEDs.

In addition to using FIrpic as a HBL or HB·ETL, we have investigated hole-blocking layers which consist of FIrpic doped into a wide gap matrix, requiring less of this particular Ir complex. In addition to the cost savings for devices with lower levels of the Ir blocker, the decreased concentration of FIrpic in the blocking layer should give improved blue color purity, relative to blue electrophosphorescent devices with a pure FIrpic blocking layer. The line broadening associated with SSSE in neat FIrpic layers is less severe in doped films, where the FIrpic-FIrpic interactions are less significant. This is clearly seen in the photoluminescent spectra of neat FIrpic and FIrpic doped thin films (Fig. 4(a)). Two doped hole-blocking matrix materials have been used: a hexaphenylene compound, SC5 (optical energy gap = 3.6 eV) [26], and OPCOT [27] (octaphenyl cyclooctatetraene C₈Ar₈, optical energy gap = 3.3 eV), shown in Fig. 2. Neither material phosphoresces at low temperature, making the estimation of their triplet energies problematic. Fortunately, SC5 is sufficiently soluble that its triplet energy can be determined by a Stern–Volmer quenching method [28], giving a triplet energy for SC5 of 2.5 eV [29]. This value is less than the triplet energy of FIrpic, suggesting that FIrpic emission from SC5 doped films results from endothermic energy transfer [11].

FIrpic emissive, double heterostructure OLEDs have been prepared with FIrpic doped OPCOT and SC5 as the HBL or HBL·ETL materials. The general structure for these devices were:ITO/NPD(300 Å)/CBP:FIrpic(6% 300 Å)/HBL(150 Å)/Alq₃(200 Å)/Mg:Ag(1000 Å)/Ag(500), whose characteristics are given in Table 2. The efficiency of the FIrpic emissive OLEDs are lower than those

Table 2
OLED performance data for devices with doped OPCOT and SC5 hole blocking layers

HBL/ETL layer structure	CIE coordinates	Turn-on voltage/V	Maximum quantum yield in %	Applied voltage (at measurement)/V
OPCOT:FirPic 15% (300 Å)	0.15 0.30	5.4	0.35	10.0
OPCOT:FirPic 15%/Alq ₃	0.18 0.36	4.3	0.77	9.1
BCP/Alq ₃	0.14 0.29	3.8	1.0	8.2
SC5:FirPic 25%/Alq ₃	0.19 0.33	4.0	1.2	8.0

The turn-on voltage is defined as the voltage required to reach an external brightness of 1 cd/m².

reported previously for related devices with a BAQ blocking layer [11], possibly due to the fabrication methods used for the present devices. That is, the current devices were exposed to air between the organic and cathode deposition steps to add the shadow mask. Aerobic exposure has been reported to markedly decrease the efficiencies of Firpic based devices [11], incorporating either BCP or BAQ HBLs. Nevertheless, all the devices discussed here were fabricated by the same method, allowing for direct comparisons of their relative performance. Here, Firpic was used as both a blue phosphorescent dopant in CBP, and as an electron conducting dopant in OPCOT or SC5. The efficiencies, turn on voltages (defined as the voltage required to reach an external brightness of 1 cd/m²) and CIE coordinates for these OLEDs are listed in Table 2. The doped HBLs give efficiencies similar to the neat Firpic-blocked devices discussed above. The efficiency of OPCOT:Firpic HBL devices were comparable to BCP HBL OLEDs, whereas the SC5:Firpic HBL device was more efficient than standard BCP HBL OLED (Table 2). In contrast to neat Firpic HBL based devices, the doped HBL devices give higher efficiencies when an Alq₃ ETL is used, suggesting that electron injection from the cathode into the doped HBL materials is less efficient than for neat Firpic.

The EL spectra of Firpic emitting OLEDs with SC5: 25% Firpic and BCP HBLs are shown in Fig. 4(b). Both the spectra and the CIE coordinates in Table 2 illustrate that the emission spectrum of the OLED utilizing a Firpic doped HBL is broader than that of the device with a BCP HBL. However, the EL spectrum of the SC5·Firpic-based device is narrower than for a device with a pure Firpic blocking layer, as expected for the doped HBL.

3.2. Electron blocking layer

While a hole-blocking layer has proven to be important for achieving high efficiency phosphorescent OLEDs, the need for a second blocking layer to prevent electron and exciton leakage into the HTL, has not often been required. The reason for this is that holes are typically more mobile than electrons in many OLED materials and the commonly used hosts for electrophosphorescent devices (i.e. carbazole derivatives) also are hole transporters. These two factors act together, resulting in a build-up of holes at the EL/ETL interface, but no electron build-up or leakage at the HTL/EL interface. When the phosphorescent dopant energy is shifted to high energy (i.e. into the blue), however, the HOMO and LUMO energies approach those of the host material, and electron leakage can become significant. The problem is illustrated in the energy level diagrams of Fig. 6. As the dopant energy levels approach the host levels, the barrier to hole injection into the luminescent layer may be comparable to the barrier to injection of electrons from the luminescent layer into the HTL, leading to substantial hole-electron recombination in the HTL. The addition of an electron blocking layer prevents electron leakage into the HTL. To achieve high efficiency and color stability for high energy electrophosphorescent devices, both electron and hole-blocking layers are therefore needed.

A family of platinum(II)(2-(4,6-difluorophenyl)pyridinato-*N,C'*) β -diketonate (e.g. FPt1 and FPt2 in Fig. 2) complexes [30] have been used to prepare blue and white emissive devices. By controlling the doping level of FPt1, it is possible to balance the emission from monomer (blue) and

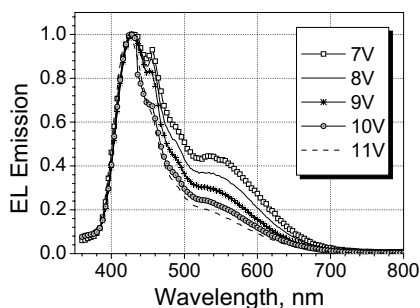


Fig. 5. Electroluminescence spectra as a function of OLED drive voltage. The device had a 6% FPt1 doped CBP emissive layer, and a device structure of ITO/NPD(400 Å)/CBP·FPt1(300 Å)/BCP (150 Å)/Alq₃(200 Å)/MgAg.

excimer (yellow–orange) emission centers, producing white electrophosphorescence [20]. The HOMO energies for both FPt monomer and excimer emitting centers are the same, falling very near the CBP HOMO energy, Table 1.² Unfortunately, while this device gave the desired white emission, the electroluminescence (EL) spectrum had a significant contribution from NPD, Fig. 5. At a bias of 7 V, both NPD ($\lambda_{\max} = 430$ nm) and monomer/excimer emission are observed, with the NPD contribution being the larger. As the bias (and hence the current) is increased, the NPD emission grows markedly. The changing percentage of NPD in the luminescence leads to poor color stability and low efficiency. The origin of the NPD emission involves electron leakage into the NPD layer. The FPt dopant and CBP HOMO energies are nearly equal (see Fig. 6 upper left), giving a barrier of roughly 0.5 eV for migration of holes from NPD into the doped luminescent layer (assuming a small interface dipole between the two materials). The barrier to electrons between the CBP and NPD (≈ 0.3 V, Table 1) is less than the hole injection barrier at the HTL/EL interface, leading to electron leakage from the EL into the NPD HTL. This problem is solved by inserting an

² The excimer does not have a bound ground state, but is formed on excitation of one of the monomer FPt1 molecules. Thus, the excimer and monomer have the same HOMO energy for device considerations, since they originate for the same states.

electron/excimer blocking layer (EBL) between the HTL and EL, preventing electron migration into the HTL as shown in Fig. 6 (right).

Blocking electron leakage can improve efficiency by balancing carrier injection into the EL, however, it is also important for the EBL to have a higher energy triplet level to prevent loss of excitons into the nonemissive adjacent HTL. Thus, the EBL must have several characteristics to be an efficient EBL: a high triplet energy, a LUMO energy sufficiently high to prevent electron leakage from the EL into the EBL and a HOMO energy that is close to that of the HTL. Two materials have been identified that meet these criteria: fac-tris(1-phenylpyrazolato,*N,C2'*)iridium(III) (Irppz) [20] and Iridium(III)bis(1-phenylpyrazolato,*N,C2'*)(2,2,6,6-tetramethyl-3,5-heptanedionato-*O,O*) ppz₂Ir(dpm). The estimated HOMO and LUMO energies of these compounds are provided in Table 1, and their chemical structures are shown in Fig. 2. The optical gaps for Irppz and ppz₂Ir(dpm) were taken from low energy edges of their absorption spectra at 3.4 and 3.1 eV, respectively. The 5.1 eV HOMO energy for Irppz was measured by UPS. Using the Irppz optical energy gap to approximate the carrier gap, we estimate the Irppz LUMO is 1.7 eV, well above the LUMOs for both CBP and the dopant. While ppz₂Ir(dpm) has similar HOMO and LUMO energies to those of Irppz, its triplet energy is significantly lower than that of Irppz, due to a low energy “Ir(dpm)” state.

When the Irppz EBL is added to the FPt2 based white emitting OLED structure, the electron leakage into the NPD layer is eliminated [31]. The structure of this device was ITO/NPD/ Irppz/CBP:FPt2/ BCP/ Alq₃/ LiF/Al. The spectra of a single dopant white emitting OLEDs (using 8 wt% FPt1 in CBP), with and without an Irppz EBL, are shown in Fig. 6. The Irppz based devices give an EL spectrum consistent with only dopant emission (i.e. no NPD emission is observed at any bias level) leading to a voltage independent white emission [20]. The peak brightness of the 10% doped device was 8000 cd/m² and the maximum quantum efficiency was $3.3 \pm 0.3\%$ (7.3 ± 0.7 lm/W) at 0.5 cd/m², dropping to $2.3 \pm 0.2\%$ (5.2 ± 0.3 lm/W) at 500 cd/m². The quantum efficiency of the device with

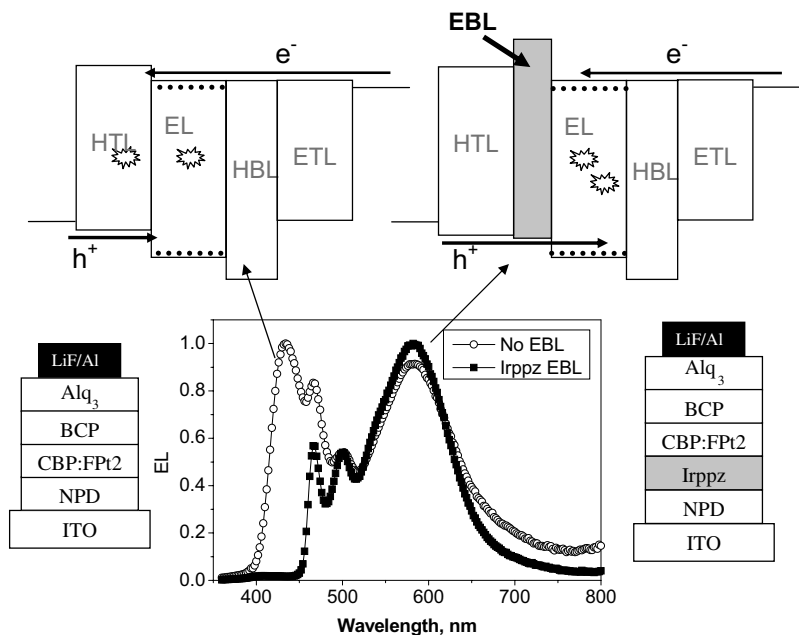


Fig. 6. Schematic energy level diagrams illustrating the role of an electron blocking layer (EBL) in an OLED. The phosphorescent dopant HOMO and LUMO levels are shown as dashed lines in the EL, close to the corresponding states in the EL (top). Excitons are indicated as starburst patterns. Electroluminescence spectra (at 10 V) and the schematic structures of the CBP:FpT2 OLEDs with and without Irppz EBL (bottom).

an Irppz blocking layer is nearly double that of the device with no EBL (peak efficiency = 1.9%). Efficiencies as high as 6.4% (12.2 lm/W, 17.0 cd/A) have been reported for monomer-excimer emitting devices [20], utilizing both electron and hole-blocking layers to confine carrier recombination and emission to the EL.

ppz₂Ir(dpm) has similar properties to Irppz, (Table 1) and also serves as an efficient EBL. Hence, it was used in FpT1:CBP based OLEDs, with results shown in Fig. 7. The ppz₂Ir(dpm) layer blocks electrons from reaching HTL, completely eliminating NPD emission from the device spectrum. A weak contribution to the EL spectrum is observed close to a wavelength of 400 nm due to residual CBP fluorescence. This is the result of a low FpT1 doping concentration that does not completely quench CBP fluorescence, and hence is not related to carrier blocking. As for the Irppz blocked devices, the EL spectrum is voltage independent. The peak quantum efficiency for the ppz₂Ir(dpm) based device is only 2.6%, compared

to 3.3% for the same device structure with Irppz used as the EBL. The lower efficiency for the ppz₂Ir(dpm) device is most likely due to less efficient exciton confinement, resulting from the lower triplet energy of ppz₂ Ir(dpm) relative to Irppz.

4. Conclusion

To achieve the highest efficiencies for electrophosphorescence based OLEDs, both carriers and excitons must be well confined within the emissive layer. While exciton formation does not necessarily need to be restricted to occur in the EL, forming the excitons in an adjacent layer and having them migrate into the EL can lead to losses and hence is avoided in the most efficient devices. The approach discussed here is to efficiently force carrier recombination and exciton confinement within the EL by the use of blocking layers. The blocking function can be incorporated as a separate layer, inserted between the EL and the HTL

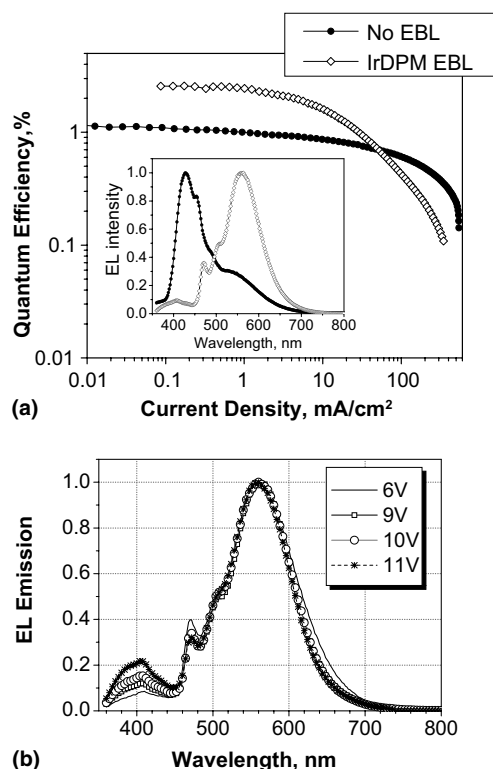


Fig. 7. (a) Quantum efficiency versus current density for FpT1-doped CBP devices with and without a ppz₂Ir(dpm) EBL(ITO/NPD(300 Å)/X(100 Å)/CBP·FpT1(300 Å)/BCP(150 Å)/Alq₃(200 Å)/MgAg), X = NPD, ppz₂Ir(dpm). The spectra of the two devices are shown in the inset. (b) EL spectra as functions of drive voltage for devices with a ppz₂Ir(dpm) EBL.

or ETL. Alternatively, the blocking function can be incorporated into the HTL or ETL materials themselves, as was shown for both BCP and FIrpic, which perform as efficient EB-ETL materials. By carefully controlling the HOMO, LUMO, and triplet energies the HTL and ETL materials, it may be possible to entirely eliminate the need for separate blocking layers at both the HTL/EL and EL/ETL interfaces. The result is a simplified structure for high efficiency electrophosphorescent devices, consisting of only three organic layers (i.e. HTL/EL/ETL). In this three layer device, the HTL and ETL materials efficiently block excitons, and conduct one charge while blocking the other. Metal complexes have great promise as serving this role as a combined carrier transport and blocking layer material.

Acknowledgements

Financial support from Universal Display Corporation and the Defense Advanced Research Projects Agency is gratefully acknowledged.

References

- [1] C.W. Tang, S.A. VanSlyke, *Appl. Phys. Lett.* 51 (12) (1987) 913.
- [2] C.W. Tang, S.A. VanSlyke, C.H. Chen, *J. Appl. Phys.* 65 (1989) 3610.
- [3] C. Adachi, M.A. Baldo, M.E. Thompson, S.R. Forrest, *J. Appl. Phys.* 90 (10) (2001) 5048.
- [4] M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, *Nature* 395 (1998) 151.
- [5] D.F. O'Brien, M.A. Baldo, M.E. Thompson, S.R. Forrest, *Appl. Phys. Lett.* 74 (1999) 442.
- [6] M.A. Baldo, S.R. Forrest, *Phys. Rev. B.* 62 (16) (2000) 10958.
- [7] M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, S.R. Forrest, *Appl. Phys. Lett.* 75 (1) (1999) 4.
- [8] C. Adachi, M.A. Baldo, S.R. Forrest, S. Lamansky, M.E. Thompson, R.C. Kwong, *Appl. Phys. Lett.* 78 (2001) 1622.
- [9] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P.E. Burrows, S.R. Forrest, M.E. Thompson, *J. Am. Chem. Soc.* 123 (2001) 4304.
- [10] C. Adachi, M. Baldo, S.R. Forrest, M.E. Thompson, *Appl. Phys. Lett.* 77 (2000) 904.
- [11] C. Adachi, R. Kwong, P. Djurovich, V. Adamovich, M. Baldo, M.E. Thompson, S.R. Forrest, *Appl. Phys. Lett.* 79 (13) (2001) 2082.
- [12] T. Watanabe, K. Nakamura, S. Kawami, Y. Fukuda, T. Tsuji, T. Wakimoto, S. Miyahuchi, *Proc. SPIE* 4105 (2001) 175.
- [13] R.C. Kwong, M.R. Nugent, L. Michalski, T. Ngo, K. Rajan, Y.J. Tung, M.S. Weaver, T.X. Zhou, M. Hack, M.E. Thompson, S.R. Forrest, J.J. Brown, *Appl. Phys. Lett.* 81 (2002) 162.
- [14] M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, Y. Taga, *Appl. Phys. Lett.* 79 (2001) 156.
- [15] X. Jiang, Z. Zhang, W. Zhao, W. Zhu, B. Zhang, S. Xu, *J. Phys. D: Appl. Phys.* 33 (2000) 473.
- [16] C. Wang, G. Jung, Y. Hua, C. Pearson, M.R. Bryce, M.C. Petty, A.S. Batsanov, A.E. Goeta, J.A.K. Howard, *Chem. Mater.* 13 (2001) 1167.
- [17] D. Kolosov, V. Adamovich, P. Djurovich, M.E. Thompson, C. Adachi, *J. Am. Chem. Soc.* 124 (2002) 9945.
- [18] J.L. Kim, J.K. Kim, H.N. Cho, D.Y. Kim, C.Y. Kim, S.I. Hong, *Macromolecules* 33 (2000) 5880.
- [19] H.S. Woo, R. Czerw, S. Webster, D.L. Carroll, J. Ballato, A.E. Strevens, D. O'Brien, W.J. Blau, *Appl. Phys. Lett.* 77 (9) (2000) 1393.

- [20] V. Adamovich, J. Brooks, A. Tamayo, A.M. Alexander, P.I. Djurovich, B.W. D'Andrade, C. Adachi, S.R. Forrest, M.E. Thompson, *New J. Chem.* 26 (2002) 1171.
- [21] S.R. Forrest, M.E. Thompson, D.D. Bradley, *Adv. Mater.* 15 (13) (2003) 1043.
- [22] N.J. Turro, *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing Co., Inc., Menlo Park, CA, 1978.
- [23] Y. Wang, N. Herron, V.V. Grushin, D. LeCloux, V. Petrov, *Appl. Phys. Lett.* 79 (4) (2001) 449.
- [24] M. Baldo, S. Lamansky, P. Burrows, M.E. Thompson, S.R. Forrest, *Appl. Phys. Lett.* 75 (1) (1999) 4.
- [25] V. Bulovic, R. Deshpande, M.E. Thompson, S.R. Forrest, *Chem. Phys. Lett.* 308 (1999) 317.
- [26] S. Cordero, M.E. Thompson, et al., The synthesis and detailed characterization of SC5 will be reported in a future publication.
- [27] P. Lu, H. Hong, G. Cai, P. Djurovich, W.P. Weber, M.E. Thompson, *J. Am. Chem. Soc.* 122 (2000) 7480.
- [28] S. Madhusoodhanan, P.I. Djurovich, T.E. Hogen-Esch, M.E. Thompson, *J. Am. Chem. Soc.* 125 (26) (2003) 7796.
- [29] S. Madhusoodhanan, M.E. Thompson, private communication.
- [30] J. Brooks, Y. Babayan, S. Lamansky, P. Djurovich, I. Tsyba, R. Bau, M.E. Thompson, *Inorg. Chem.* 41 (12) (2002) 3055.
- [31] B. D'Andrade, J. Brooks, V. Adamovich, M.E. Thompson, S.R. Forrest, *Adv. Mater.* 14 (15) (2002) 1032.