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White Stacked Electrophosphorescent Organic Light-Emitting Devices Employing MoO_3 as a Charge-Generation Layer**

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High-efficiency white organic light-emitting devices (OLEDs)^[1–4] are of interest due to their potential uses in full-color active-matrix displays coupled with color filters, and also as solid-state lighting sources. For full-color display backlights, high brightness is required because of loss of light in the optical films and the small aperture ratio ($\sim 40\%$) in the backplane of the thin-film transistors.^[5] Similarly, high brightness ($> 800 \text{ cd m}^{-2}$) is required for solid-state lighting sources. To achieve both high brightness and efficiency, the stacked OLED (SOLED)^[6–8] consisting of multiple electroluminescent elements connected in series has been introduced. More recently, high-efficiency green-light-emitting SOLEDs have been demonstrated. These devices use a transparent charge-generating interlayer such as indium tin oxide (ITO),^[9] V_2O_5 ,^[9] or an organic p–n junction,^[10] where the hole-transporting layer (HTL) and electron-transporting layer (ETL) are doped with FeCl_3 and Li, respectively. In the SOLED structure, the luminance at a fixed current density increases linearly with the number of stacked and independent OLED elements. This can lead to a significant improvement in lifetime, as well as external efficiency, by reducing the degradation that accompanies the high drive currents required to achieve similarly high brightness in a single-element OLED.

Here we demonstrate high-efficiency white-light-emitting SOLEDs based on phosphorescent emitters with Li-doped ETLs. To the best of our knowledge, it is the first report using a vacuum-thermally deposited MoO_3 film interposed between stacked elements. Figure 1 shows the transmittance of a layer of MoO_3 . The film is more transparent in the wavelength range from 400 to 500 nm compared with previously reported V_2O_5 interlayers,^[11,12] which is essential to achieve an efficient

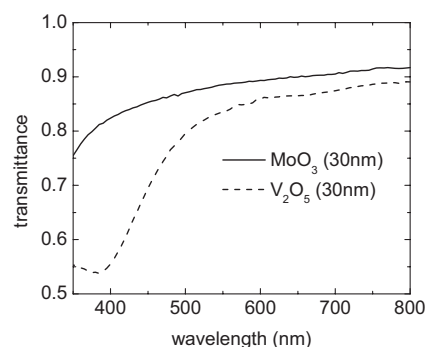


Figure 1. Transmittance spectrum of a 30 nm thick MoO_3 layer compared to that of a 30 nm thick V_2O_5 layer. Both films were thermally evaporated.

white SOLED. Furthermore, it is easier to handle than the corrosive and optically absorbing FeCl_3 . To our knowledge, this also is the first device that utilizes phosphor with pyrazolyl-based ligands, which provides a blue–green emission, in a white-light-emitting OLED.

Figure 2 shows the proposed energy diagram of the white electrophosphorescent SOLED consisting of multiple, nearly identical white-light-emitting OLED elements, or subpixels. The highest occupied molecular orbital (HOMO) energies for each material were measured using UV photoemission spectroscopy, and the position of the lowest unoccupied molecular orbital (LUMO) energies were estimated by adding the energy corresponding to the onset of optical absorption to the HOMO energy. This procedure generally leads to a systematic underestimation of the HOMO–LUMO energy gap by 0.5 to 1.0 eV. In the white SOLED, two or three electrophosphorescent subpixels are stacked (corresponding to a 2- or 3-SOLED, respectively), with the thickness of the 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl (NPD) HTL varying in each element. To obtain both high efficiency and balanced emission intensity from each phosphor required to achieve the desired white color temperature (5500 K), it is crucial to i) effectively confine the carriers and excitons within the emission layers (EMLs) of each subpixel in the stack, ii) ensure that all exciton formation occurs within each EML, and iii) control optical interference and weak microcavity effects.^[13] In our devices, varying the NPD thickness determines the total optical path length through the stack. Given that the charge mobility of NPD is roughly 100 times higher than in the other organic materials used, its thickness variation ($< 100 \text{ nm}$) does not significantly affect the drive voltage nor

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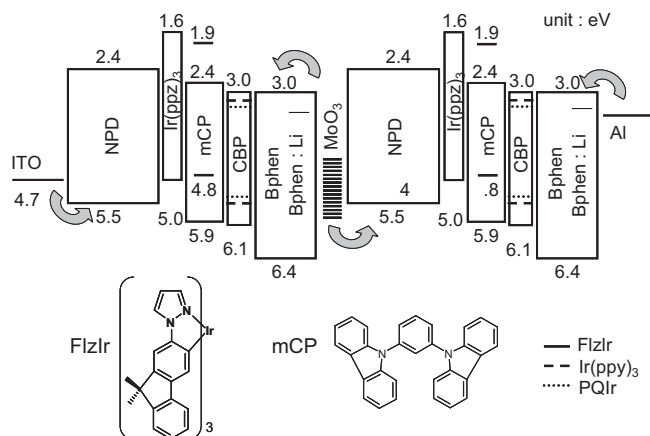


Figure 2. Top: Proposed energy-level diagram of a white SOLED with two electrophosphorescent elements. Numbers indicate the respective highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO, respectively) energies relative to vacuum. The HOMO and LUMO energies of Ir(ppz)₃ and PQIr are (5.1 eV, 2.6 eV) and (5.0 eV, 2.7 eV), respectively. The arrows indicate the carrier injection from electrodes and the MoO₃ charge-generation layer. Bottom: The molecular structures of Ir(flz)₃ and mCP. NPD: 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl; CBP: 4,4'-N,N'-dicarbazole-biphenyl; Bphen: 4,7-diphenyl-1,10-phenanthroline; Ir(ppz)₃: *fac*-tris(1-phenylpyrazolyl-*N,C*^{2'})iridium(III); Ir(ppy)₃: *fac*-tris(2-phenylpyridinato-*N,C*^{2'})iridium(III); PQIr: iridium(III) bis(2-phenylquinolyl-*N,C*^{2'})acetylacetonate.

the carrier balance and, hence, the position of the recombination zone.^[14]

We employ *fac*-tris(1-(9,9-dimethyl-2-fluorenyl)pyrazolyl-*N,C*^{2'})iridium(III) (Ir(flz)₃) as a blue-green phosphor^[15] doped at 10 wt.-% into a *N,N'*-dicarbazolyl-3,5-benzene (mCP) host.^[16] Here, the Ir(flz)₃ LUMO is at 1.9 eV, and the HOMO at 4.8 eV, referenced to vacuum. The low HOMO energy of Ir(flz)₃ relative to that of mCP suggests that Ir(flz)₃ is a hole trap. Electron injection into Ir(flz)₃ directly from the secondary host, 4,4'-*N,N'*-dicarbazole-biphenyl (CBP), is energetically unfavorable. Exciton formation, therefore, occurs by direct excitation of the triplet, either by injection from the CBP LUMO, or by electron transfer from the mCP LUMO. The shallow LUMO level is at least 0.5 eV above those of mCP and CBP, as well as the other dopants, thus preventing electron leakage from the EML into the adjacent layers. Furthermore, *fac*-tris(1-phenylpyrazolyl-*N,C*^{2'})iridium(III) (Ir(ppz)₃) and 4,7-diphenyl-1,10-phenanthroline (Bphen), with wider energy gaps than those of the phosphors and host materials, act as barriers to exciton and charge diffusion across the EML/HTL and EML/ETL interfaces, respectively. The use of blockers maintains charge balance within each EML, since the Li-doped Bphen/MoO₃ more efficiently generates electrons than holes.

In the EML adjacent to the layer comprised of Ir(flz)₃:mCP, the green-light-emitting phosphor, *fac*-tris(2-phenylpyridinato-*N,C*^{2'})iridium(III) (Ir(ppy)₃) is co-doped with the red phosphor, iridium(III) bis(2-phenylquinolyl-*N,C*^{2'})acetylacetonate (PQIr) in CBP to enhance the energy transfer from the host to PQIr.^[2]

Here the concentrations of Ir(ppy)₃ and PQIr are 3 and 10 wt.-%, respectively. The majority of excitons in this region are generated by direct trapping on both PQIr and Ir(flz)₃.

Figure 3a shows the electrophosphorescence spectra of a 2-SOLED with the NPD thickness in the top element between the MoO₃ interlayer and the Al cathode being varied from 40 to 100 nm in 20 nm steps. The Ir(flz)₃ emission be-

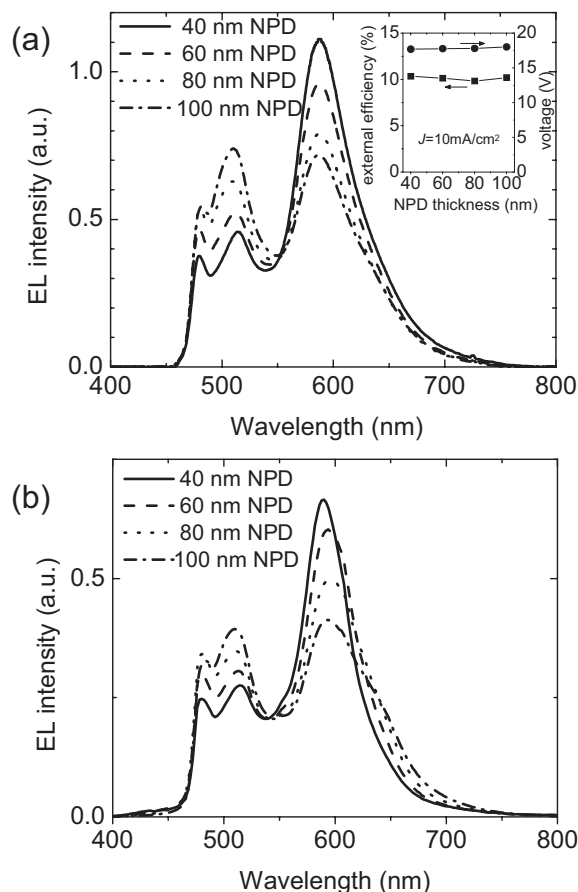


Figure 3. a) Electrophosphorescence spectra at current density, $J = 10 \text{ mA cm}^{-2}$ of white SOLEDs with the following structures: NPD (40 nm)/Ir(ppz)₃ (10 nm)/mCP:10 wt.-% Ir(flz)₃ (20 nm)/CBP:3 wt.-% Ir(ppy)₃:10 wt.-% PQIr/Bphen (20 nm)/Bphen:Li (1:1 molar ratio) (20 nm)/MoO₃ (10 nm)/NPD (x nm)/Ir(ppz)₃ (10 nm)/mCP:10 wt.-% Ir(flz)₃ (20 nm)/CBP:3 wt.-% Ir(ppy)₃:10 wt.-% PQIr/Bphen (20 nm)/Bphen:Li (1:1 molar ratio) (20 nm)/Al (50 nm). NPD thickness (x) was varied as shown. Inset: External efficiency (squares) and operation voltage (circles) at $J = 10 \text{ mA cm}^{-2}$ as a function of NPD thickness. b) Calculated electrophosphorescence spectra for devices with the same structure as that measured in (a); EL: electroluminescence.

comes more intense with increasing thickness of the NPD layer, while the operational voltage and external efficiencies are not significantly changed (see inset, Fig. 3a). Here, “external efficiency” (as distinct from quantum efficiency), is defined as the ratio of the total number of photons emitted by the OLED into the forward-viewing direction to the number of electrons injected from the cathode.

Figure 3b shows the results of optical simulations of the spectra for the 2-SOLEDs shown in Figure 3a. The refractive indices (n) of ITO and MoO₃ in the visible region employed in the simulation were measured by ellipsometry to be 1.9 and 2.2, respectively. Due to the index differences with the organic films ($n=1.7$), weak microcavity effects are expected. In the simulation, we considered the SOLED as a stratified structure consisting of isotropic and homogeneous layers with plane-parallel interfaces. A transfer-matrix method was then employed to describe normal propagation through each layer.^[13] The optically simulated spectra in Figure 3b are in reasonable agreement with the experimental results in Figure 3a, indicating that the changes in spectra with NPD thickness are dominated by optical interference and weak microcavity effects, rather than by carrier transport and exciton diffusion.

The external and luminous power efficiencies of 1-, 2-, and 3-SOLEDs are shown in Figure 4a. The corresponding device structures and their performances are summarized in Table 1. The maximum forward-viewing external efficiencies for 1-, 2-, and 3-SOLEDs are $\eta_{\text{ext}}=13.6\pm1.2\%$ at a

suitable illumination fixtures,^[2,17] the 1-, 2- and 3-SOLEDs therefore have total external and power efficiencies at an approximate forward-surface luminance of 500 cd m^{-2} of $\eta_{\text{ext,tot}}=10.9\pm1.0\%$, $\eta_{\text{p,tot}}=11.2\pm1.0\text{ lm W}^{-1}$; $\eta_{\text{ext,tot}}=28.6\pm2.2\%$, $\eta_{\text{p,tot}}=18.5\pm1.4\text{ lm W}^{-1}$; and $\eta_{\text{ext,tot}}=51.0\pm3.2\%$, $\eta_{\text{p,tot}}=20.7\pm1.4\text{ lm W}^{-1}$, respectively.

We find that the maximum external efficiencies of the 1-, 2- and 3-SOLEDs are approximately proportional to the number of subpixels over a wide range of current densities.^[8] For example, the maximum η_{ext} of the 2- and 3-SOLEDs are, respectively, 1.8 and 2.6 times that of a conventional OLED with a similar structure,^[1] indicating that the transparent internal floating electrode efficiently generates both electrons and holes. The maximum external efficiency shifts toward increasing current density as the number of subpixels increases. Note that the luminous power efficiency of the 3-SOLED is lower than that of comparable 1- and 2-SOLEDs at low current densities as a result of a drop in intensity at a wavelength of 550 nm for the 3-SOLED.

Figure 4b compares the current density versus voltage characteristics of the various structures. As expected, the drive voltage at fixed J increases with the number of subpixels. Note that Li doping of Bphen allows for efficient electron injection and, hence, a high external efficiency. When undoped Bphen was placed adjacent to MoO₃, the external and power efficiencies were lowered and the drive voltage was raised dramatically compared to its Li-doped counterpart (see Table 1). These results suggest inefficient charge generation, resulting from the absence of the combination of the insulating MoO₃ and the Li-doped Bphen.

Figure 5 shows the electrophosphorescence spectra of 1-, 2-, and 3-SOLEDs at $J=10\text{ mA cm}^{-2}$. We infer that the pronounced change in the spectrum of the 3-SOLED (and its resulting decrease in luminous efficiency, see Fig. 4) is a consequence of optical effects, as discussed above. The dependence of the spectrum on J of the 3-SOLED is shown in the inset of Figure 5, indicating a blue-shift at high J due to a charge imbalance in the three subpixels. Commission Internationale de L'Eclairage chromaticity coordinates for the 1-, 2-, and 3-SOLEDs are ($x=0.37$, $y=0.46$), ($x=0.39$, $y=0.45$), and ($x=0.35$, $y=0.44$), respectively, as shown in Table 1. The color shift at high current densities is found to be very small, as shown in the inset of Figure 5.

In summary, we have demonstrated high-efficiency white electrophosphorescent devices consisting of stacked white electrophosphorescent OLEDs with a blue-green phosphor separated by thin and transparent MoO₃ charge-injecting interlayers. The external efficiencies approximately scale with the number of white-light-emitting subpixels. The SOLEDs reach a maximum forward-viewing efficiency of $\eta_{\text{ext}}=34.9\pm2.2\%$ for a 3-SOLED and total external efficiency of $\eta_{\text{ext,tot}}=51.0\pm3.2\%$ at a luminance of 500 cd m^{-2} . The forward-viewing and total power efficiencies are relatively independent of the number of elements in the stack, peaking at $\eta_{\text{p}}=28.9\pm2.2\text{ lm W}^{-1}$ ($\eta_{\text{p,tot}}=18.5\pm1.4\text{ lm W}^{-1}$) and $22.7\pm1.4\text{ lm W}^{-1}$ ($\eta_{\text{p,tot}}=20.7\pm1.4\text{ lm W}^{-1}$) for 2- and

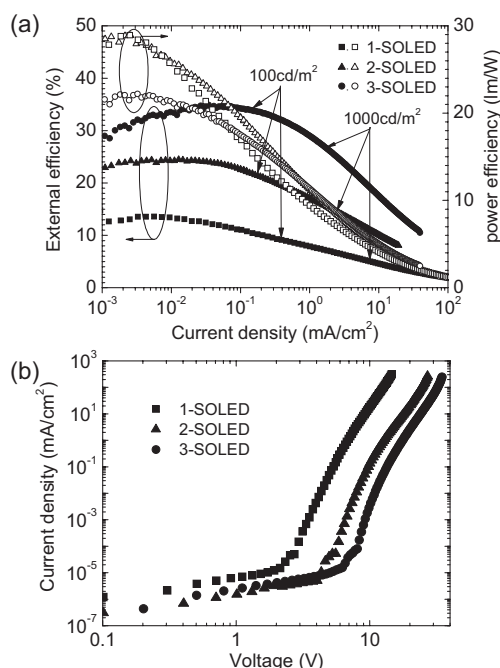


Figure 4. a) Forward-viewing external and luminous power efficiencies of 1-, 2-, and 3-SOLEDs as functions of J . The arrows indicate values at brightnesses of 100 and 1000 cd m^{-2} , as measured in the forward-viewing direction. b) Current-voltage characteristics of 1-, 2-, and 3-SOLEDs.

current density of $J=0.0056\text{ mA cm}^{-2}$ (with a power efficiency of $\eta_{\text{p}}=28.9\pm2.5\text{ lm W}^{-1}$ at $J=0.0025\text{ mA cm}^{-2}$), $\eta_{\text{ext}}=24.7\pm1.9\%$ at $J=0.012\text{ mA cm}^{-2}$ ($\eta_{\text{p}}=28.9\pm2.2\text{ lm W}^{-1}$ at $J=0.0026\text{ mA cm}^{-2}$), and $\eta_{\text{ext}}=34.9\pm2.2\%$ at $J=0.035\text{ mA cm}^{-2}$ ($\eta_{\text{p}}=22.7\pm1.4\text{ lm W}^{-1}$ at $J=0.0032\text{ mA cm}^{-2}$), respectively. Since illumination sources are typically characterized by their total emitted power when placed in

Table 1. Characteristics of white SOLEDs. CIE: Commission International de l'Eclairage; η_{ext} : forward-viewing external efficiency; η_{p} : power efficiency.

Device	Structure [a]	η_{max} [%]	$\text{Max}\eta_{\text{p}}$ [lm W ⁻¹]	Max. efficiency [cd A ⁻¹]	Voltage at $J = 10$ [V]	CIE co-ordinates at $J = 10$	Color rendering index
1-SOLED	EPa	13.6 ± 1.2	28.9 ± 2.5	34.9 ± 3.1	9.2	(0.36, 0.46)	62
2-SOLED	EPa/MoO ₃ /EPb	24.7 ± 1.9	28.9 ± 2.2	66.6 ± 5.0	18.0	(0.39, 0.45)	64
3-SOLED	EPa/MoO ₃ /EPc/MoO ₃ /EPc	34.9 ± 2.2	22.7 ± 1.4	77.0 ± 5.0	24.1	(0.35, 0.44)	66
2-SOLED-a [b]	EPa/MoO ₃ /EPb	9.8 ± 1.0	4.5 ± 0.5	21.9 ± 2.2	32.6	(0.53, 0.43)	56

[a] EP=electrophosphorescent subpixel element consisting of NPD (variable thickness)/Ir(ppz)₃ (10 nm)/10 wt.-% FlzIr:mCP (20 nm)/10 wt.-% PQIr:3 wt.-% Ir(ppy)₃:CBP (5 nm)/Bphen (20 nm)/Bphen:Li (1:1 molar ratio) (20 nm). The NPD thickness in each EL element is for EPa 40nm, EPb 100nm, and EPc 60nm.

[b] The EP element has Bphen (20 nm) instead of Bphen:Li (20 nm) adjacent to MoO₃.

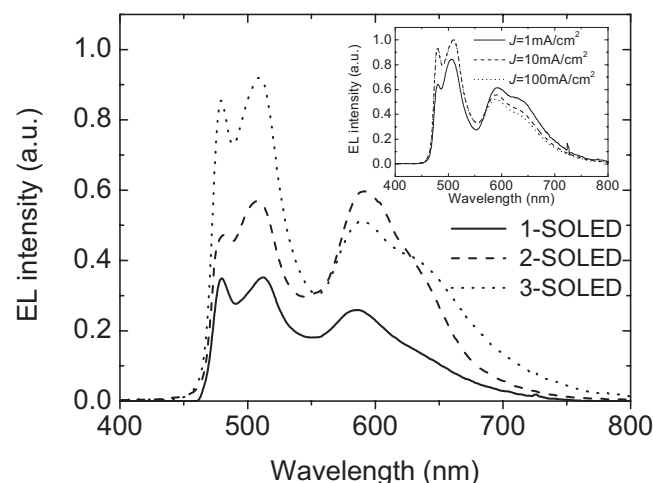


Figure 5. Electrophosphorescence spectra of 1-, 2-, and 3-SOLEDs at a current density of $J = 10 \text{ mA cm}^{-2}$. Inset: EL spectra of a 3-SOLED at $J = 1, 10, \text{ and } 100 \text{ mA cm}^{-2}$.

3-SOLEDs, respectively. The use of both electron- and hole-blocking layers, combined with a MoO₃/Li-doped Bphen charge-generation layer, ensures a uniform white color balance for each subpixel in the stack, along with very high efficiency for charge injection. These results demonstrate that white electrophosphorescent SOLEDs are a promising means for achieving high brightness and efficient sources for indoor lighting and display backlights.

Experimental

The SOLED was grown on a glass substrate pre-coated with a 150 nm thick, $\sim 20 \Omega \text{ sq}^{-1}$ ITO layer. Prior to organic-film deposition, the ITO-coated substrates were degreased with detergent solution and solvents, and then exposed to UV-ozone at $\sim 20 \text{ mW cm}^{-2}$ for 5 min prior to loading into a vacuum evaporation system with a base pressure of 10^{-7} torr (1 torr ≈ 133 Pa). All organic materials were purified by temperature-gradient sublimation in vacuum prior to use. Each identical subpixel structure was started with deposition of NPD of various thicknesses (40, 60, 800, and 100 nm), followed by the 10 nm thick Ir(ppz)₃ exciton-blocking layer, a 20 nm thick blue-green EML, a 5 nm thick red EML capped by an ETL consisting of a 20 nm thick Bphen layer, followed by a second 20 nm thick Bphen layer mixed with Li in a 1:1 molar ratio. All organic layers were sequentially grown at a rate of 1 to 5 $\text{\AA s}^{-1}$ without breaking vacuum. Each subpixel

in the stack was separated by a thermally deposited, 10 nm thick MoO₃ charge-generation layer. Finally, a 50 nm thick Al cathode layer was deposited on the surface through a shadow mask with an array of circular, 1.0 mm diameter openings. Masking for cathode deposition was completed in a glove box with <1 ppm water and oxygen. During NPD deposition in the upper and lower subpixels, two blade masks were translated in vacuum to form a thickness staircase in otherwise identical devices to systematically test the dependence of HTL thickness on device performance.

Current-voltage and external efficiency measurements were carried out using a semiconductor parameter analyzer (HP-4145B) and a calibrated Si photodiode (Hamamatsu S3584-08) following standard procedures [18].

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