

Efficient, deep-blue organic electrophosphorescence by guest charge trapping

R. J. Holmes, B. W. D'Andrade, and S. R. Forrest^{a)}

Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering and the Princeton Materials Institute, Princeton University, Princeton, New Jersey 08544

X. Ren, J. Li, and M. E. Thompson

Department of Chemistry, University of Southern California, Los Angeles, California 90089

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We demonstrate efficient, deep-blue organic electrophosphorescence using a charge-trapping phosphorescent guest, iridium(III) bis(4',6'-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate (FIr6) doped in the wide-energy-gap hosts, diphenyldi(o-tolyl)silane (UGH1) and *p*-bis(triphenylsilyl)benzene (UGH2), where exciton formation occurs directly on the guest molecules. Charge trapping on the guest is confirmed by the dependence of the drive voltage and electroluminescence spectrum on guest concentration. Ultraviolet photoemission spectroscopy measurements establish the relative highest occupied molecular orbital positions of FIr6 in UGH1 and UGH2. Peak quantum and power efficiencies of $(8.8 \pm 0.9)\%$ and (11.0 ± 1.1) lm/W in UGH1 and $(11.6 \pm 1.2)\%$ and (13.9 ± 1.4) lm/W in UGH2 are obtained, while the emission in both cases is from FIr6 and is characterized by Commission Internationale de l'Eclairage coordinates of $(x=0.16, y=0.26)$ in UGH2. © 2003 American Institute of Physics. [DOI: 10.1063/1.1624639]

Recently, efficient blue electrophosphorescence in organic light-emitting devices (OLEDs) has been generated by energy transfer from a fluorescent host to a phosphorescent guest molecule.^{1–3} However, there are obstacles to using energy transfer to excite deeper blue guest phosphors. As the energy gap of the guest becomes large, successively larger host energy gaps are required to maintain efficient exothermic energy transfer from host to guest.² While finding such hosts is possible, electrically injecting carriers and forming excitons on wide-gap materials is often difficult, requiring the traversing of large energy barriers between carrier transport layers and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the wide-gap host. To alleviate this difficulty, we employ host molecules that act as an inert matrix, leaving the guest molecules to both conduct and trap charge, allowing for direct exciton formation on the guest phosphor. This eliminates the need to electrically excite the host, while allowing for efficient carrier collection, exciton formation, and recombination at the guest molecular sites. For efficient emission, however, an exothermic path from host to guest must be maintained to eliminate the transfer of excitons formed on guest molecules back to the lower energy host molecules.^{1,2}

A number of studies have examined means to distinguish between the two primary mechanisms of exciton formation and emission in OLEDs: host–guest energy transfer and direct charge trapping followed by exciton formation at the guest. Distinctions between these mechanisms can be made from the dependence of drive voltage or changes in output spectrum on guest concentration, as will be shown subsequently.^{4–6}

OLEDs were grown on a glass substrate precoated with a ~ 100 -nm-thick layer of indium tin oxide (ITO) having a sheet resistance of $\sim 20 \Omega/\square$. Substrates were degreased

with solvents and then cleaned by exposure to a UV-ozone ambient. All organic layers were grown in succession without breaking vacuum ($\sim 1 \times 10^{-7}$ Torr). Masking for cathode deposition after the layers were deposited was completed in a glove box with <1 ppm water and oxygen. The device structure consisted of a 40-nm-thick 4-4'-bis [*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl (NPD) hole transport layer, followed by a 15-nm-thick layer of *N,N'*-dicarbazolyl-3,5-benzene (mCP)⁷ that confines excitons to the OLED emissive layer (EML). The 25-nm-thick blue EML consists of bis(4',6'-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate⁸ (FIr6) codeposited with either diphenyldi(o-tolyl)silane (UGH1) or *p*-bis(triphenylsilyl)benzene (UGH2). Finally, a 40-nm-thick electron transporting and hole blocking layer consisting of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, BCP) was deposited. Literature procedures were used to prepare NPD,⁹ mCP,⁷ UGH1,^{10,11} UGH2,¹² and FIr6,⁸ while BCP was purchased from the Aldrich Chemical Company.¹³ All materials were purified by repeated temperature gradient vacuum sublimation. Cathodes consisting of a 0.5-nm-thick layer of LiF followed by a 50-nm-thick layer of Al were patterned using a shadow mask with an array of 1-mm-diameter circular openings. Current–voltage and external efficiency measurements were carried out using standard methods.¹⁴

Figure 1 shows the chemical structures and the emission and excitation spectra measured for the host and guest materials used. The room-temperature emission spectra for UGH1, UGH2, and FIr6 were collected under illumination by a Hg lamp monochromated to wavelengths of $\lambda = 239, 230,$ and 325 nm, respectively. The excitation spectra of UGH1, UGH2, and FIr6 were collected for emission wavelengths of 303, 320, and 458 nm, respectively. The blue phosphorescence of FIr6 is readily visible at room temperature, allowing for assignment of the triplet state to the peak

^{a)}Electronic mail: forrest@ee.princeton.edu

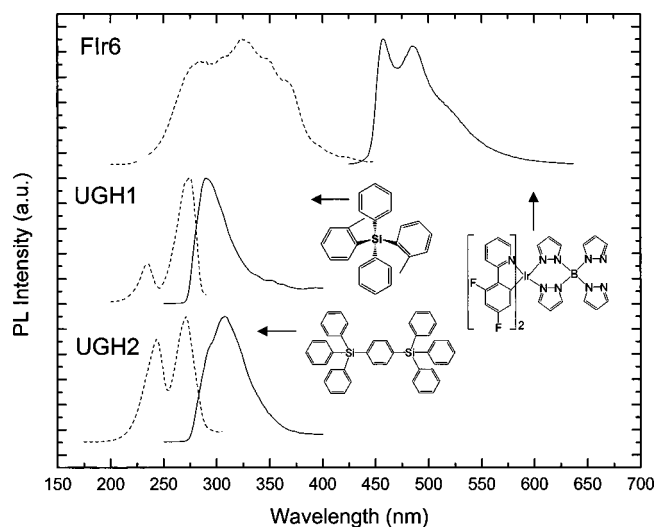


FIG. 1. Room-temperature emission and excitation spectra and the chemical structures of the emissive materials used in this study. Emission spectra (solid lines) were collected under excitation at $\lambda=239$, 230, and 325 nm, for UGH1, UGH2, and FIr6, respectively, while excitation spectra (broken lines) were collected at $\lambda=303$, 320, and 458 nm.

at $\lambda=457$ nm. The phosphorescence of each fluorescent host is measured in 2-methyltetrahydrofuran solution at 77 K to be $\lambda=393$ nm for UGH1 and $\lambda=390$ nm for UGH2. From these energies, we expect the energy transfer to FIr6 from both UGH1 and UGH2 to be exothermic.

Figure 2 depicts the performance of two phosphorescent OLEDs, one with UGH1 (closed symbols) and the other with UGH2 (open symbols) codeposited with FIr6. Peak external electroluminescent (EL) quantum and power efficiencies of $\eta_{\text{EXT}}=(8.8\pm0.9)\%$ and $\eta_p=(11.0\pm1.1)$ lm/W for a UGH1:10% FIr6 (by weight) OLED are achieved at current densities of 22.5 and 6.2 $\mu\text{A}/\text{cm}^2$, respectively. With a UGH2 host also doped with 10% FIr6, $\eta_{\text{EXT}}=(11.6\pm1.2)\%$ and $\eta_p=(13.9\pm1.4)$ lm/W are obtained at current densities of 9.9 and 5.6 $\mu\text{A}/\text{cm}^2$, respectively. Devices using UGH1 and UGH2 have luminances of 12 600 cd/m^2 (320 mA/cm^2) and 11 800 cd/m^2 (156 mA/cm^2), respectively, at 15 V. The

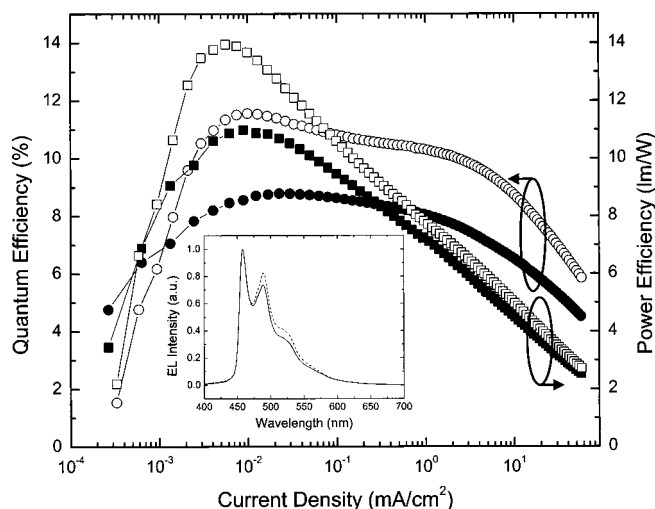


FIG. 2. Quantum (circles) and power (squares) efficiency versus drive current density for ITO/NPD (40 nm)/mCP (15 nm)/UGH1 (closed symbols) or UGH2 (open symbols): 10% FIr6 (25 nm)/BCP (40 nm)/LiF (0.5 nm)/Al (50 nm) OLEDs. **Inset:** EL at 10 mA/cm^2 originating solely from FIr6 in UGH1 (broken line) and UGH2 (solid line).

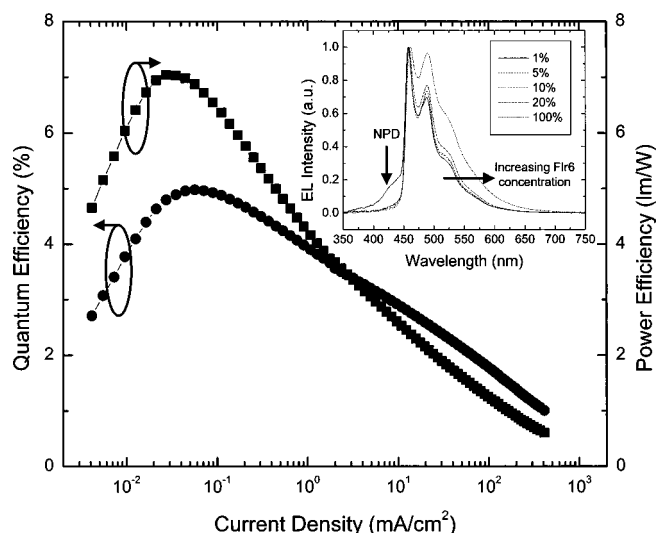


FIG. 3. Quantum (circles) and power (squares) efficiency versus drive current density for ITO/NPD (40 nm)/mCP (15 nm)/FIr6 (25 nm)/BCP (40 nm)/LiF (0.5 nm)/Al (50 nm) OLEDs. **Inset:** Dependence of the EL spectrum on guest concentration at 10 mA/cm^2 for various concentrations of FIr6 in UGH2. For FIr6 concentrations less than 5%, incomplete electron trapping by FIr6 is evidenced by the observation at $\lambda=435$ nm of NPD emission.

difference in efficiency between UGH1 and UGH2 devices is possibly due to the enhanced dopant aggregation in UGH1, leading to increased exciton quenching in this device. The tendency to aggregate is inferred from the strong peak in quantum efficiency for UGH1:FIr6 devices between 5% and 10% FIr6, compared to the nearly concentration-independent efficiency of UGH2:FIr6 devices between 5% and 20% dopant concentrations.

The inset of Fig. 2 shows the EL spectra at 10 mA/cm^2 originating from FIr6, with Commission Internationale de L'Eclairage (CIE) coordinates of (0.16, 0.28) and (0.16, 0.26) for UGH1 and UGH2 devices, respectively. The EL spectra were independent of drive current density from 1 to 100 mA/cm^2 .

In all devices, a thin layer of mCP is inserted between the NPD layer and the EML. Without the mCP, the EL spectrum shows a significant contribution from NPD, and the device efficiency drops by an order of magnitude. Here, mCP efficiently prevents the leakage of both excitons and electrons from the EML into NPD, increasing color purity and carrier balance in the emissive layer.

To determine whether charge transport is influenced by the presence of the guest, we fabricated an OLED consisting of a neat FIr6 EML, whose quantum and power efficiencies are shown in Fig. 3. The peak efficiencies are $\eta_{\text{EXT}}=(5.0\pm0.5)\%$ and $\eta_p=(7.0\pm0.7)$ lm/W, comparable to other highly efficient devices whose emissive zone consists of a neat layer of phosphorescent material.¹⁵ The CIE coordinates at 10 mA/cm^2 are (0.19, 0.34), with a slight blueshift with increasing drive current density. The high efficiencies observed for devices with a neat layer of FIr6 suggest that this dopant can efficiently transport charge without the need for a host.

We also fabricated devices consisting only of a neat layer of UGHx. We find that $\eta_{\text{EXT}}=(0.9\pm0.1)\%$ and $\eta_p=(0.4\pm0.1)$ lm/W for both UGH1 and UGH2, with emission originating almost entirely from the NPD hole transport layer.

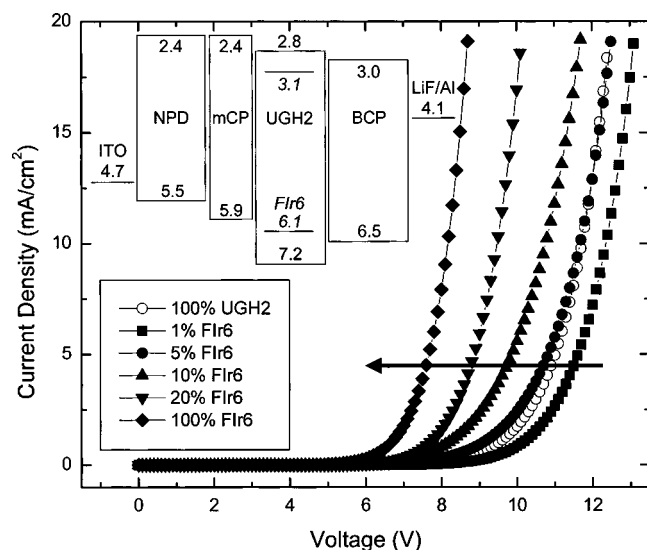


FIG. 4. J - V characteristics for ITO/NPD (40 nm)/mCP (15 nm)/UGH2: x % Flr6 (25 nm)/BCP (40 nm)/LiF (0.5 nm)/Al (50 nm) OLEDs. The arrow points in the direction of increasing Flr6 concentration. **Inset:** Proposed energy level scheme for the device under zero applied bias.

layer. This suggests that UGH1 and UGH2 are effective hole blocking materials, although both molecules transport electrons, allowing for exciton formation to occur on NPD, as observed.

Figure 4 shows the current-density-voltage (J - V) characteristics of a UGH2:Flr6 device as a function of Flr6 concentration, as well as a proposed energy level scheme for the device. The HOMO energies for each material were measured using ultraviolet photoemission spectroscopy, except those of BCP and NPD, which were taken from Ref. 16. The LUMO energies were estimated by adding the energy corresponding to the onset of optical absorption to the HOMO energy. While this yields an underestimate of the carrier transport gap, the accuracy of the relative energy level placements for all of the organic materials considered is sufficient to understand device performance.¹⁶ From Fig. 4, we infer a barrier to hole injection into UGH2 from mCP of 1.3 eV (consistent with the observation of NPD emission in a neat UGH2 device), while hole injection into Flr6 is energetically favorable with only a 0.2 eV barrier. This is supported in the J - V characteristics of doped device. The increase in drive voltage with a low (1%) concentration of Flr6 results since Flr6 acts as an electron trap in the EML.⁶ In a device consisting of undoped UGH2, current is carried by electrons in the EML, allowing for exciton formation and recombination directly on NPD. The addition of Flr6 traps reduces the electron mobility while also increasing hole injection from NPD/mCP into the EML. This is inferred from the inset of Fig. 3, where a significant component of the EL spectrum ($\lambda \leq 450$ nm) from a UGH2:1% Flr6 device originates from NPD. As the concentration of Flr6 is increased, the hole injection efficiency into the EML increases, while electron leakage into NPD decreases as electrons are trapped by the guest molecules. A further increase in Flr6 concentration beyond 5% leads to a decreasing drive voltage, with the minimum drive voltage at 100% Flr6. Thus, for guest concentrations $>5\%$, both electrons and holes are transported by Flr6, with UGH2 acting as an inert host matrix.

The same trends are also observed for UGH1:Flr6-based devices. However, for UGH1, the increase in voltage at 1% Flr6 is larger, remaining larger than for neat UGH1 even at 5% Flr6. Increases in concentration beyond 5% Flr6 lead to drive voltages similar to those for UGH2 in Fig. 4. This behavior is consistent with the LUMO level difference for UGH1:Flr6 being larger than for UGH2:Flr6. For UGH1, the HOMO is at (7.2 ± 0.2) eV, and the LUMO energy is at (2.6 ± 0.4) eV, yielding a LUMO difference with Flr6 of 0.5 eV, reduced to only 0.3 eV for UGH1. Hence, Flr6 is a more effective electron trap in UGH1.

We have demonstrated highly efficient blue electrophosphorescence by charge trapping on guest molecules of Flr6 doped into the wide-energy-gap hosts UGH1 and UGH2. The EL of Flr6 in a host-guest system is noticeably "bluer" in color at (0.16, 0.26) than the previously studied phosphorescent blue emitter iridium(III)bis[(4,6-difluorophenyl)pyridinato- $N, C^{2'}$]picolate (Flrpic), which has CIE coordinates of (0.16, 0.37).² In Ref. 2, efficient blue electrophosphorescence from Flrpic is demonstrated using exothermic energy transfer from a wide-gap host to the Flrpic guest, although this mechanism is more difficult to achieve for deep-blue emitters. The deep HOMO levels of UGH1 and UGH2 make hole trapping on Flr6 the dominant means for hole injection into the EML. The direct formation of excitons on Flr6 avoids electrical excitation of the wide-gap host, while eliminating exothermic back transfer from guest to host.

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- C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **79**, 2082 (2001).
- R. J. Holmes, S. R. Forrest, Y.-J. Tung, R. C. Kwong, J. J. Brown, S. Garon, and M. E. Thompson, *Appl. Phys. Lett.* **82**, 2422 (2003).
- S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki, and F. Sato, *Appl. Phys. Lett.* **83**, 569 (2003).
- M. Uchida, C. Adachi, T. Koyama, and Y. Taniguchi, *J. Appl. Phys.* **86**, 1680 (1999).
- X. J. Wang, M. R. Andersson, M. E. Thompson, and O. Inganäs, *Synth. Met.* **137**, 1019 (2003).
- H. Murata, C. D. Merritt, and Z. H. Kafafi, *IEEE J. Sel. Top. Quantum Electron.* **4**, 119 (1998).
- V. Adamovich, J. Brooks, A. Tamayo, A. M. Alexander, P. Djurovich, B. W. D'Andrade, C. Adachi, S. R. Forrest, and M. E. Thompson, *New J. Chem.* **26**, 1171 (2002).
- J. Li, P. I. Djurovich, B. D. Alleyne, I. Tsyba, N. N. Ho, R. Bau, and M. E. Thompson (unpublished).
- D. E. Loy, B. E. Koene, M. E. Thompson, P. E. Burrows, and S. R. Forrest, *Chem. Mater.* **10**, 2235 (1998).
- H. Gilman and G. N. R. Smart, *J. Org. Chem.* **15**, 720 (1950).
- M. Charisse, A. Zickgraf, H. Stenger, E. Brau, C. Besmarquet, M. Drager, S. Gerstmann, D. Dakternieks, and J. Hook, *Polyhedron* **17**, 4497 (1998).
- H. Gilman and G. D. Lichtenwalte, *J. Am. Chem. Soc.* **80**, 608 (1958).
- Bathocuproine, Cat. 14,091-0, Sigma-Aldrich Corp., St. Louis, Missouri.
- S. R. Forrest, D. D. C. Bradley, and M. E. Thompson, *Adv. Mater. (Weinheim, Ger.)* **15**, 1043 (2003).
- Y. Wang, N. Herron, V. V. Grushin, D. LeCloux, and V. Petrov, *Appl. Phys. Lett.* **79**, 449 (2001).
- I. G. Hill and A. Kahn, *J. Appl. Phys.* **86**, 4515 (1999).