A Dibenzofuran-Based Host Material for Blue Electrophosphorescence
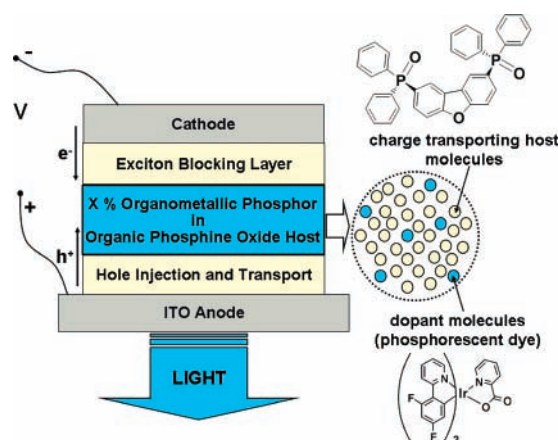
Paul A. Vecchi, Asanga B. Padmaperuma, Hong Qiao, Linda S. Sapochak,* and Paul E. Burrows

Material Science Division, Pacific Northwest National Laboratory, Richland, Washington 99352

linda.sapochak@pnl.gov

ABSTRACT

Dibenzofuran (DBF) is converted to a vacuum-sublimable, electron-transporting host material via 2,8-substitution with diphenylphosphine oxide moieties. Close π–π stacking and the inductive influence of P=O moieties impart favorable electron-transport properties without lowering the triplet energy. A maximum external quantum efficiency of 10.1% and luminance power efficiency of 25.9 lm/W are realized using this material as the host for the blue-green electrophosphorescent molecule, iridium(III) bis(4,6-(di-fluorophenyl)pyridinato-*N,C²'*)picolinate (FIrpic).

Currently, the most efficient organic light-emitting devices (OLEDs) are based on organic electrophosphorescence, where an organometallic phosphor is physically doped into a conductive organic host matrix and electroluminescence (EL) from the dopant results from energy transfer from the host and/or direct trapping of charge on the phosphor.[1,2] Highly efficient and long-lived red and green phosphorescent OLEDs have been demonstrated.[3] However, efficient and stable blue electrophosphorescence remains a challenge in part because of the lack of appropriate organic charge transporting host materials with a triplet energy (E_T) high enough to prevent quenching of the dopant emission (ideally ~3 eV). Such a high E_T requires either a very small molecule with poor thermal stability or one with a short conjugation length defined by saturated centers such as Si.[4]

We recently reported that both 4,4′-bis(diphenylphosphine oxide)biphenyl and 2,7-bis(diphenylphosphine oxide)-9,9-dimethylfluorene function as wide band gap and charge-transporting host materials for the sky blue phosphorescent dopant, iridium(III) bis(4,6-(di-fluorophenyl)pyridinato-*N,C²'*)picolinate (FIrpic) in OLEDs with peak quantum efficiencies of ~8% and low drive voltages.[5,6] For both materials, the phosphine oxide (P=O) moieties act as points of saturation between the "active" chromophore bridge (fluorene or biphenyl) and outer phenyl groups resulting in materials with high triplet energies characteristic of the bridges, but with physical properties suitable for device

(1) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *J. Appl. Phys.* **2001**, *90*, 5048.

(2) Holmes, R. J.; D'Andrade, B. W.; Forrest, S. R.; Ren, X.; Li, J.; Thompson, M. E. *Appl. Phys. Lett.* **2003**, *83*, 3818.

(3) Kwong, R. C.; Weaver, M. S.; Lu, M.-H. M.; Tung, Y.-J.; Chwang, A. B.; Zhou, T. X.; Hack, M.; Brown, J. J. *Org. Electron.* **2003**, *4*, 155.

fabrication by thermal sublimation. However, both these bridges have triplet energies comparable to the phosphorescent dopant FIrpic (E_T = 2.7 eV), which may limit the device quantum efficiency due to back transfer of excitons from the dopant to the host molecules.

In this paper, we show that the higher triplet energy (E_T = 3.1 eV) building block, dibenzofuran (DBF), when substituted at the 2,8-positions with diphenylphosphine oxide groups serves as a more efficient charge-transporting host for blue electrophosphorescent OLEDs than similar molecules built using hydrocarbon bridges.

Synthesis of 2,8-bis(diphenylphosphine oxide)dibenzofuran (3) was accomplished by a modified literature procedure outlined in Scheme 1.[7] The starting material, 2,8-dibromo-

Scheme 1
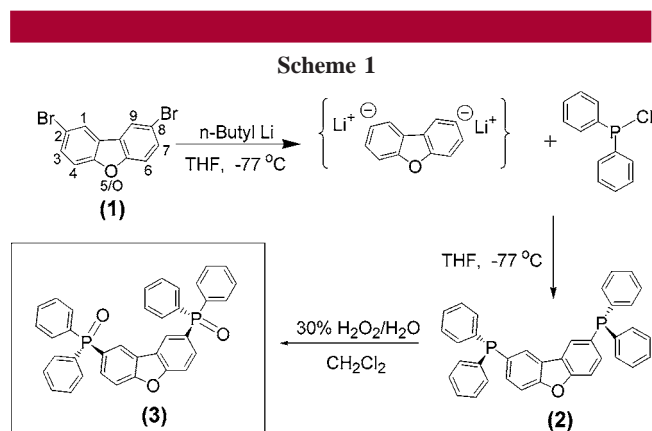
dibenzofuran (1) was obtained by addition of Br_2 (2.1 equiv) to DBF in $CHCl_3$. Compound 1 was rigorously purified to remove isomeric impurities by repeated solvent washings followed by multiple sublimations in a tube furnace ($\sim10^{-7}$ Torr) until the product was pure by ^{1}H NMR. A lithium–halogen exchange reaction between 1 and n-butyllithium (2 equiv) in THF (−77 °C, Ar) followed by reaction with chlorodiphenylphosphine (2 equiv) gave crude 2,8-bis-(diphenylphosphine)dibenzofuran (2). The diphosphine product was rigorously purified by solvent washings and by column chromatography. Compound 2 was then oxidized with an excess of 30% H_2O_2 to give 3 as a white solid. Compound 3 was purified by multiple sublimations in a three-zone tube furnace to give the final purified product subliming at 250−255 °C ($\sim10^{-7}$ Torr). Complete spectroscopic and structural characterization of compounds 1−3 is reported in the Supporting Information.

The structure of 3 was confirmed by single-crystal X-ray diffraction from a sample obtained by sublimation (see Figure 1 and Supporting Information). Similar to organic diphosphine oxides reported previously,[6,8] P═O bond lengths are identical [1.480(2) Å] and all P−C bond lengths are similar

(4) Ren, X.; Li, J.; Holmes, R. J.; Djurovich, P. I.; Forrest, S. R.; Thompson, M. E. *Chem. Mater.* **2004**, *16*, 4743.

(5) Burrows, P. E.; Padmaperuma, A. B.; Sapochak, L. S.; Djurovich, P.; Thompson, M. E. *Appl. Phys. Lett.* **2006**, *88*, 183503.

(6) Padmaperuma, A. B.; Sapochak, L. S.; Burrows, P. E. *Chem. Mater.* **2006**, *18*, 2389.

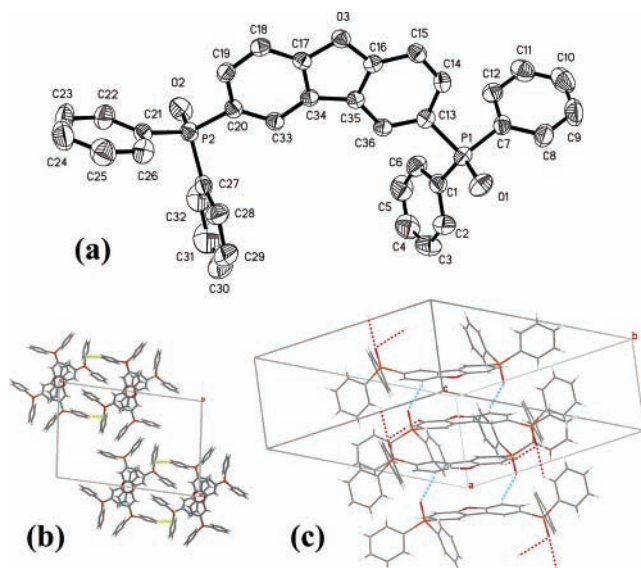(7) Baldwin, R. A.; Cheng, M. T. *J. Org. Chem.* **1967**, *32*, 1572.

Figure 1. (a) Thermal ellipsoid plot (ORTEP) for 3. Ellipsoids shown at the 50% probability level and hydrogen atoms omitted for clarity. Crystal packing showing (b) view down the *b*-axis, with edge-to-face interactions indicated in yellow and (c) side view of 1-dimensional $\pi-\pi$ stacking facilitated by one P(2)−O(2)- - -H(15)−C(15) (cyan dashed lines) and two P(1)−O(1)- - -H(18 & 12)-C (18 & 12) (red dashed lines) H-bonding interactions.

($\sim$1.81 Å). The P═O groups are oriented antiparallel in a transoid conformation with respect to the DBF plane with O−P−C−C torsion angles of 79.19° and 86.80° for P(1)−O(1) and P(2)−O(2), respectively. Close π- - -π interactions (3.385 Å) are observed between the DBF bridges in 3, forming 1-dimensional arrays along the *b*-axis (see Figure 1b) facilitated by two close P−O- - -H−C interactions (all C- - -O distances $\sim$3.4 Å) with the DBF ring on adjacent molecules (see Figure 1c). Although 3 exhibits strong $\pi-\pi$ stacking in the crystal, thermal analysis (DSC, 10 K/min, N_2) showed stable glass formation with T_g of 105 °C and no crystallization exotherm.

Computational modeling (B3LYP/6-31G*) predicts that Ph_2P═O substitution of DBF at the 2,8-positions does not significantly change the energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) but lowers the energy of each by 0.39 and 0.44 eV, respectively. These predictions correspond well with the minimal difference observed between the absorption energy onsets for DBF (4.06 eV) and 3 (4.02 eV). The experimental absorption spectra are shown in Figure 2, where the absorption maximum of 3 (290 nm, log ϵ = 4.26) is shown to be slightly red shifted from the absorption of the unsubstituted DBF bridge because of the inductive influence of the P═O moieties. The solid-state absorbance of 3 is also shown in Figure 2 and is similar to the solution spectrum.

The fluorescence spectrum of 3 was independent of solution polarity and is approximately the mirror image of

(8) Fie, Z.; Kocher, N.; Mohrschladt, C. J.; Ihmels, H.; Stalke, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 783.
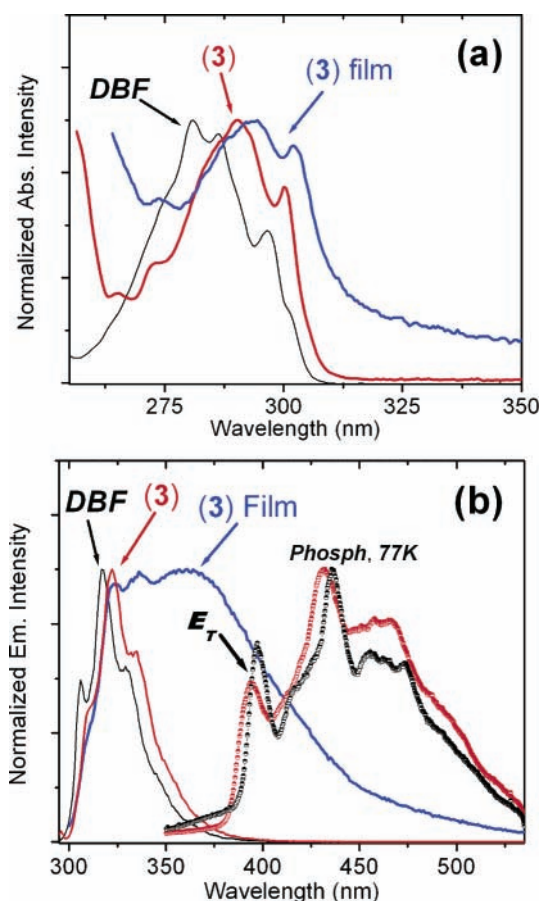
Figure 2. Absorption (a) and emission (λ_{exc} = 290 nm, rt); (b) spectra of DBF (black line) and **3** (red line) in CH$_2$Cl$_2$ ($\sim$10^{-5} M) compared to a 400 Å thick vapor deposited film of **3** (blue line). Phosphorescence spectra of DBF (black circles) and **3** (red circles) (77 K, CH$_2$Cl$_2$, λ_{exc} = 280 nm, delay time 300 μs) are also shown in (b) with $v_{0,0}$ peak used to determine triplet energy identified with arrow.

A CH$_2$Cl$_2$ glass containing **3** at 77 K exhibits phosphorescence peaking at 431 nm with a $v_{0,0}$ peak at 395 nm, corresponding to a high E_T of 3.14 eV, which is almost identical to the triplet energy of DBF (E_T = 3.12 eV) (see Figure 2b). The P=O moieties slightly reduce the triplet lifetime of **3** (τ_{phos} = 3.05 ± 0.06 s) compared to the unsubstituted DBF bridge (τ_{phos} = 4.1 s),[10] which can be attributed to weak spin−orbital coupling with the phosphorus atom.

To evaluate **3** as a host material for blue electrophosphorescence, OLEDs were fabricated with the shortest wavelength commercially available phosphorescent dopant, FIrpic, doped at 10% and 20% by mass via coevaporation with **3**. The device structure grown on ITO glass (<15 Ω/square) by thermal evaporation as described previously[5,6] was composed of 100 Å copper phthalocyanine (CuPc)/200 Å N,N′-diphenyl-N,N′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (α-NPD)/50 Å 4,4′,4″-tris(carbazol-9-yl)triphenylamine (TCTA)/200 Å 10 or 20% FIrpic in (**3**)/200 Å (**3**)/6 Å LiF/1000 Å Al. Compound **3** served both as electron-transporting host in the emissive layer and as an exciton blocking layer in this device configuration.

As shown in Figure 3 (inset), only FIrpic emission is observed in the both the EL spectrum from the device and
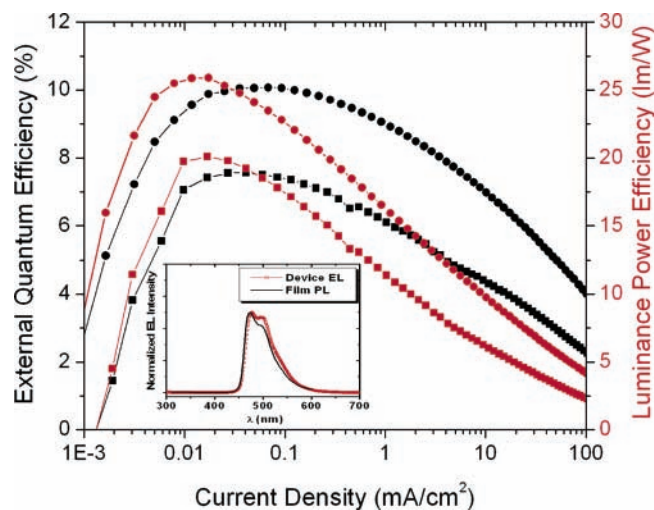
the absorption spectrum with UV emission at λ_{max} (em) = 322 nm and a small Stokes shift (3427 cm^{-1}), similar to the unsubstituted DBF bridge (318 nm, 4140 cm^{-1}, respectively) (see Figure 2b). The fluorescence quantum yield measured in CH$_2$Cl$_2$ vs quinine sulfate was 0.44 with a singlet lifetime of 3.2 ± 0.5 ns. Although the solid-state film of **3** exhibited similar structured emission in the UV, a new broad emission peak centered at 361 nm was also observed. Excitation spectra indicated that both the structured UV emission and broad lower energy emission originated from the same ground state, suggesting that the latter was excimer emission. This emission was much weaker in solution and only observed by subtraction of a lower concentration (2×10^{-6} M) spectrum from a higher concentration (2×10^{-5} M) spectrum revealing a broad peak at 355 nm, which is similar to excimer emission at 360 nm reported for DBF at high solution concentration.[9]

Figure 3. Comparison of the external quantum efficiencies (black) and luminance power efficiencies (red) for OLEDs with 10% (squares) and 20% (circle) Firpic doped into PO14. Inset: device EL spectrum and film PL spectrum for 20% FIrpic in compound **3**.

the PL spectrum from a 20% FIrpic in compound **3** film prepared by thermal evaporation. Hence, complete energy transfer to the phosphorescent dopant occurs with no measurable spectral effects due to excimers of **3**. The external quantum efficiency (η_{ex}) and luminous power efficiency (η_p) of these devices are also depicted in Figure 3, and all device results are summarized in Table 1. Using 20% FIrpic in compound **3**, a maximum η_{ex} of 10.1% at 70 μA/cm^2 and

(9) Pinion, J. P.; Minn, F. L.; Filipescu, N. *J. of Lumin.,* **1971**, *3*, 245 and Wang, X.; Tian, J.; Kofron, W. G.; Lim, E. C. *J. Phys. Chem. A* **1999**, *103*, 1560.

(10) Davydov, S. N.; Rodionov, A. N.; Shigorin, D. N.; Syutkina, O. P.; Krasnova, T. L. *Russ. J. Phys. Chem.* **1981**, *55*, 444.

Table 1. Device Properties

device property[a]	10% FIrpic	20% FIrpic
$\eta_{ex,max}$ (%) [J, mA/cm^2]	7.6 (0.04)	10.1 (0.07)
$\eta_{c,max}$ (cd/A)	20.2	26.9
V_{opt} @ max QE	3.3	3.6
$\eta_{p,max}$ (lm/W) [J, mA/cm^2]	20.1 (0.02)	25.9 (0.02)
η_{ex}[b] (%) [J, mA/cm^2]	4.7 (6.4)	8.0 (3.8)
η_c[b] (cd/A)	12.4	21.2
η_p[b] (lm/W)	7.0	12.5
V_{opt}[b] (V)	5.6	5.4

[a] $\eta_{ex,max}$, maximum external QE; $\eta_{c,max}$, maximum luminance efficiency; $\eta_{p,max}$, maximum luminance power efficiency; and V_{opt}, operating voltage at a specified current. [b] Reported at 800 cd/m^2.

3.6 V was obtained. As the drive current was increased to a brightness of 800 cd/m^2 the η_{ex} dropped to 8.0% at 5.4 V. The measured luminous efficiencies were 26.9 cd/A and 21.2 cd/A, respectively. Assuming Lambertian emission into π steradians, the corresponding derived power efficiencies were 25.9 and 12.5 lm/W.

These device properties of OLEDs incorporating **3** as an host for FIrpic are superior to those reported previously using other organic diphosphine oxide host materials (i.e., analagous diphosphine compounds with biphenyl and fluorene bridges).[5,6] Specifically, a larger η_{ex} is realized and maintained at higher drive current and similar low operating voltages (~5.4 V at 800 cd/m^2) are achieved. The higher device external quantum efficiency is attributed to the higher triplet energy of the DBF bridged phosphine oxide derivative (**3**) and consequent prevention of back energy transfer between host and dopant molecule. Further, the morphological stability of **3** is greater than both the biphenyl or fluorene bridged counterparts (i.e., higher T_g and no recrystallization exotherm). However, previous studies of furan-based optoelectronic materials, including polyfurans[11] and benzofuran oligomers[12] have reported poor photooxidative stability of the furan ring. Preliminary studies of compound **3** films also showed some photobleaching on long-term exposure to UV excitation (~254 nm) in the presence of air (see the Supporting Information). More detailed stability studies and testing on devices appropriately encapsulated for long operating lifetimes are currently being investigated.

In conclusion, P=O moieties were used to electronically isolate a high triplet energy DBF bridge allowing the photophysical properties to be incorporated into a vacuum sublimable material (**3**) for OLED applications. While other schemes for increasing the triplet energy of organic host materials have been published, the resulting loss of molecular conjugation length invariably raises the operating voltage of the blue OLEDs. The ability of **3** and other organic diphosphine oxide compounds to combine high E_T with low operating voltage devices is attributed to the inductive effect of the P=O moieties, and subsequent energy lowering of the LUMO resulting in enhancement of both electron injection and transport in the device. The overall result is a device with EQE > 10% at high brightness but V_{op} < 5.5 V compared to literature voltages of ~10 V. Given the >3 eV triplet energy of **3**, we expect similar high efficiency and low voltage results from shorter wavelength organometallic phosphors as they become available.

Supporting Information Available: Detailed experimental and computational procedures, NMR and X-ray structural information (CIF), and crystal structure data. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0614121

(11) Saadeh, H.; Goodson, T., III; Yu, L. *Macromolecules* **1997**, *30*, 4608; Politis, J. K.; Nemes, J. C.; Curtis, M. D. *J. Am. Chem. Soc.* **2001**, *123*, 2537.

(12) Anderson, S.; Taylor, P. N.; Verschoor, G. L. B. *Chem.—Eur. J.* **2004**, *10*, 518.