

## The study of new host materials for solution-processed green organic electrophosphorescence

**Sung-Hyun Jung\*, Ho-Jae Lee, Young-Hoon Kim, Hyung-Sun Kim, Eun-Sun Yu, Mi-Young Chae, Tu-Won Chang**

Cheil Industries Inc., 332-2 Gocheon-Dong, Uiwang-Si, Gyeonggi-Do 437-711, Korea  
TEL: 82-31-596-4667, E-mail: ematerial.jung@samsung.com

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### Abstract

We report the syntheses, photophysical properties and device performances of solution processible host material for green-phosphorescent OLEDs. The butterfly-shaped new host materials with nonconjugated linkage of carbazole and fluorene moieties have large triple energy band gap around 2.8 eV. All of the EL devices exhibited turn-on voltages in the range of 4.8-5.0 V. GH-4 exhibited the best performance with a maximum current efficiency and power efficiency of 21.1 cd/A and 7.9 lm/W.

### 1. Introduction

Organic electrophosphorescent diodes have attracted considerable interest because of the benefit of high efficiency compared with fluorescent materials [1-3]. The high efficiency of electrophosphorescent diodes can be achieved by harvesting both singlet and triplet excitons, contrary to fluorescent organic materials which harvest only singlet excitons. So far, most of the high-performance OLEDs based on small molecules are fabricated by multilayer vacuum thermal evaporation [4-5]. Progress in solution processed electrophosphorescent diodes is often lagging behind due to lack of suitable host materials. One of the requirements for soluble host materials is to form morphologically stable and uniform amorphous thin films with tens of nanometer thickness. Furthermore, for achieving efficient electrophosphorescence from the triplet guest in a host matrix, the triplet band gap energy of the host has to be larger than that of the guest to facilitate exothermic energy transfer from the host to the guest and to prevent reverse energy transfer from the guest back to the host [6]. Therefore, the development of effective host materials for triplet emitters imposes some challenges to molecular designs. In this work, we report butterfly-like molecular design having wide triplet band gap energy, adopting the nonconjugated linkage of carbazole and fluorene units. Furthermore,

these materials revealed bulky molecular structure and showed outstanding thermal and morphological stabilities.

### 2. Experimental

Absorption spectra of polymer solution and film were recorded with a HP 8453 UV-vis spectrometer. Photoluminescence spectra were obtained with a HITACHI F-4500 spectrophotometer. Differential scanning calorimetry (DSC) was carried out under a nitrogen atmosphere at a heating rate of 20 °C/min on a Thermal Analyzers DSC2910. The device structure was ITO/PEDOT:PSS(50 nm)/GH host:TPBI(1:1):Ir(mppy)<sub>3</sub> 13% (50 nm)/TPBI(30 nm)/LiF(1 nm)/Al(100 nm). The Current-Voltage characteristics of the devices were measured using Keithley 2400 electrometer. The brightness was measured using chromometer CS-1000A (Minolta).

### 3. Results and discussion

The chemical structures of new host materials under investigation are shown in Figure 1. Two classes of materials are studied, including the 3, 6-linked oligomers with *ter*-butyl phenyl (GH-1, GH-2) and with triphenyl amine (GH-3, GH-4) at centered carbazole 9-position. All the materials show high decomposition temperatures ( $T_d$ ) over 500 °C, and distinct glass transitions with 248 °C, 278 °C, 236 °C, and 263 °C, respectively. Thermal and morphological stabilities of organic EL materials play an important role in OLEDs. The excellent thermal stability with high  $T_d$  and  $T_g$  indicates high morphological stability, which is favorable to improve OLEDs performance and lifetime during operation.

The photophysical and electrochemical properties of all the compounds are summarized in Table 1. All

the materials showed the large spectral overlap with the absorption of MLCT of Ir(mppy)<sub>3</sub> (Figure 2). Thus, efficient singlet energy transfer (Föster transfer) from each host to Ir(mppy)<sub>3</sub> is expected. In order to test the efficiency of energy transfer, thin films of GH-1/TPBI (1:1), GH-2/TPBI (1:1), GH-3/TPBI (1:1), and GH-4/TPBI (1:1) with different concentrations (1wt%: 4 wt%, 7 wt%, 13 wt%) of Ir(mppy)<sub>3</sub> were prepared and optically excited.

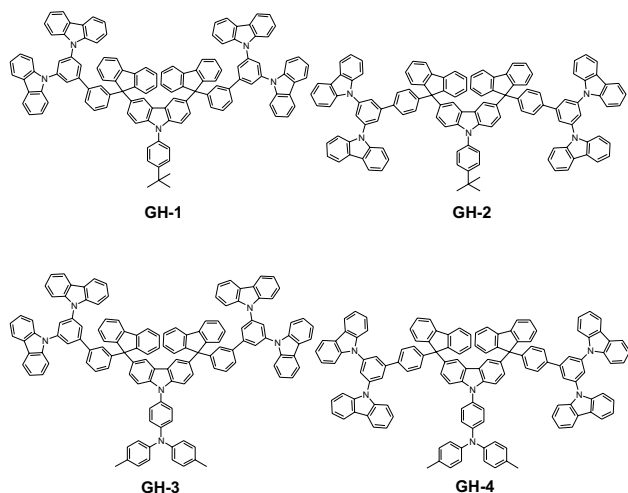


Figure 1. Chemical structures of soluble host materials under investigation.

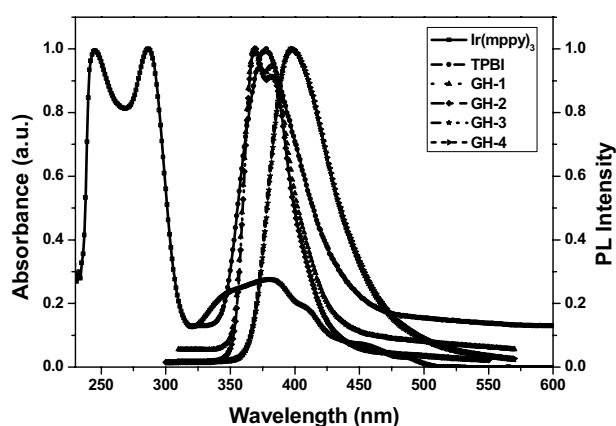


Figure 2. Absorption spectrum of the film of Ir(mppy)<sub>3</sub> and emission spectra of GH-1, GH-2, GH-3, GH-4, and TPBI.

The PL spectra of the films with different concentrations of Ir(mppy)<sub>3</sub> excited at 300 nm are shown in Figure 3. The PL profile contains two peaks: one around at 380 nm, which results from the emission of co-hosts and the other at 508 nm with a shoulder at 540 nm, which results from the triplet

emission of Ir(mppy)<sub>3</sub>. The emission intensity at 380 nm reduced significantly even with 1% concentration of Ir(mppy)<sub>3</sub>. At 4% concentration, the emission observed from co-host is very weak and the emission from Ir(mppy)<sub>3</sub> is completely dominant. Therefore, efficient Föster energy transfer from co-hosts to the dopant is confirmed by the dominant emission from the dopant. For evaluating the capability of the materials as a host for electrophosphorescent device, phosphorescence of the materials in solution was also checked at 77 K.

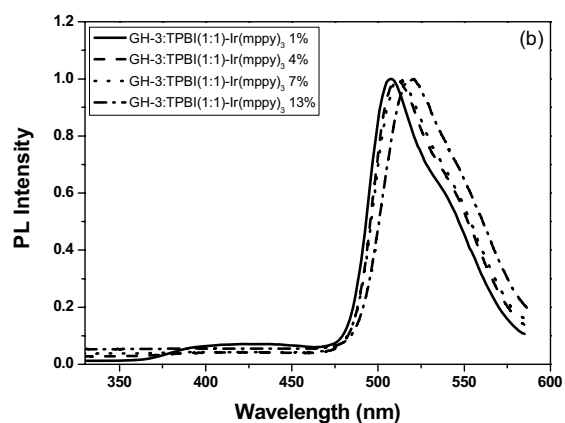
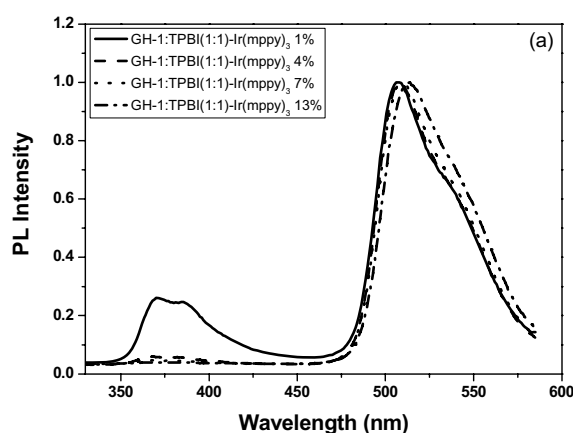


Fig. 3. Photoluminescent spectra of thin films of (a) GH-1:TPBI(1:1) and (b) GH-3:TPBI(1:1) with different concentrations (1 wt%, 4 wt%, 7 wt%, 13 wt%) of Ir(mppy)<sub>3</sub>.

Figure 4 shows the phosphorescence spectra of the materials, which exhibit a maximum at 431 nm, 446 nm, 434 nm, and 446 nm, corresponding to the triplet energy gap of 2.87 eV, 2.78 eV, 2.85 eV, and 2.78 eV, respectively. Such triplet energy gaps indicate that the materials are suitable as host materials for Ir(mppy)<sub>3</sub>,

which has triplet energy gap of about 2.4 eV.

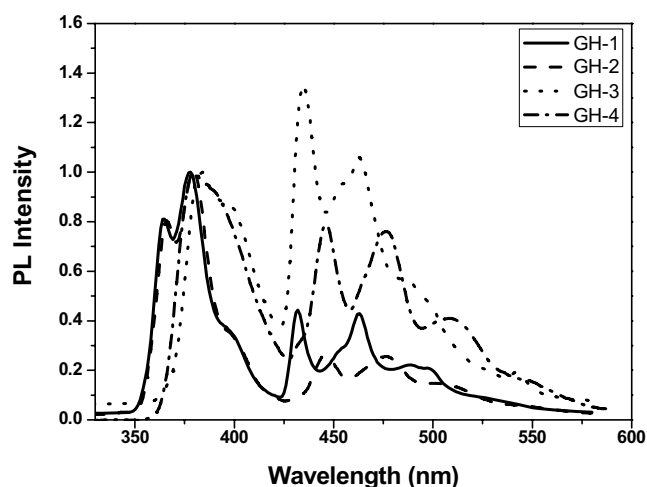


Fig. 4. Emission spectra of the compounds GH-1, GH-2, GH-3, and GH-4 in 2-methyl THF at 77 K.

TABLE 1. Summary of the physical and electrochemical properties of the host materials.

Materials	Flou. ( $\lambda_{\max}$ ) (nm)	Phos. ( $\lambda_{\max}$ ) (nm) <sup>a</sup>	$E_{\text{triplet}}$ (eV) <sup>b</sup>	HOMO (eV) <sup>c</sup>	LUMO (eV)
GH-1	369	431	2.87	-5.74	-2.20
GH-2	369	446	2.78	-5.76	-2.22
GH-3	397	434	2.85	-5.31	-1.77
GH-4	397	446	2.78	-5.32	-1.79

(a) Phosphorescence peak in solutions ( $1 \times 10^{-5}$  in 2-methyl THF, 77 K).

(b) Triplet energy estimated from the highest-energy phosphorescence peak.

(c) Deduced from electrochemical potentials under the assumption that the energy level of ferrocene was -4.8 eV versus vacuum level.

With high triplet energies, these butterfly-shaped molecules are considered as promising soluble hosts for green electrophosphorescence, and they have been subjected to electrophosphorescence studies using multilayer devices on indium tin oxide (ITO). Poly(3,4-ethylene dioxythiophene) (PEDOT) was used to promote the hole injection and poly(2,7-(9,9-di-*n*-octylfluorene)-alt-(1,4-phenylene-4-*sec*-butyl phenyl)imino)-1,4-phenylene) (TFB) served as an interlayer between PEDOT:PSS and emissive layer. The interlayer prevents the exciton quenching at the

PEDOT:PSS interface, resulting in a significant improvement in the device efficiency of OLEDs. 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) served as a hole and exciton blocker, while LiF and Al acted as an electron injection layer and a cathode. The butterfly-shaped materials and TPBI doped with Ir(mppy)<sub>3</sub> served as an emitting layer. TPBI was also used electron transporter in the emissive layer. The EL devices were fabricated with the structure of ITO/PEDOT:PSS(50 nm)/GH host:TPBI(1:1):Ir(mppy)<sub>3</sub> 13% (50 nm)/TPBI(30 nm)/LiF(1 nm)/Al(100 nm). The electroluminescence (EL) characteristics of the devices are summarized in Table 2.

TABLE 2. Summary of the characteristics of devices.

Hosts	Turn-on (V)	$L_{\max}^a$ (cd/m <sup>2</sup> )	$\eta_{\text{c max}}^b$ (cd/A)	$\eta_{\text{p max}}^c$ (lm/W)	$\eta_{\text{c}}$ at 2000 cd/m <sup>2</sup> (cd/A)
GH-1	5.0	10400 (10.6 V)	18.7	6.6	17.8
GH-2	5.0	11620 (10 V)	19.6	7.5	18.7
GH-3	4.8	12690 (10 V)	18.9	7.0	14.4
GH-4	5.0	10170 (9.6 V)	21.1	7.9	19.8

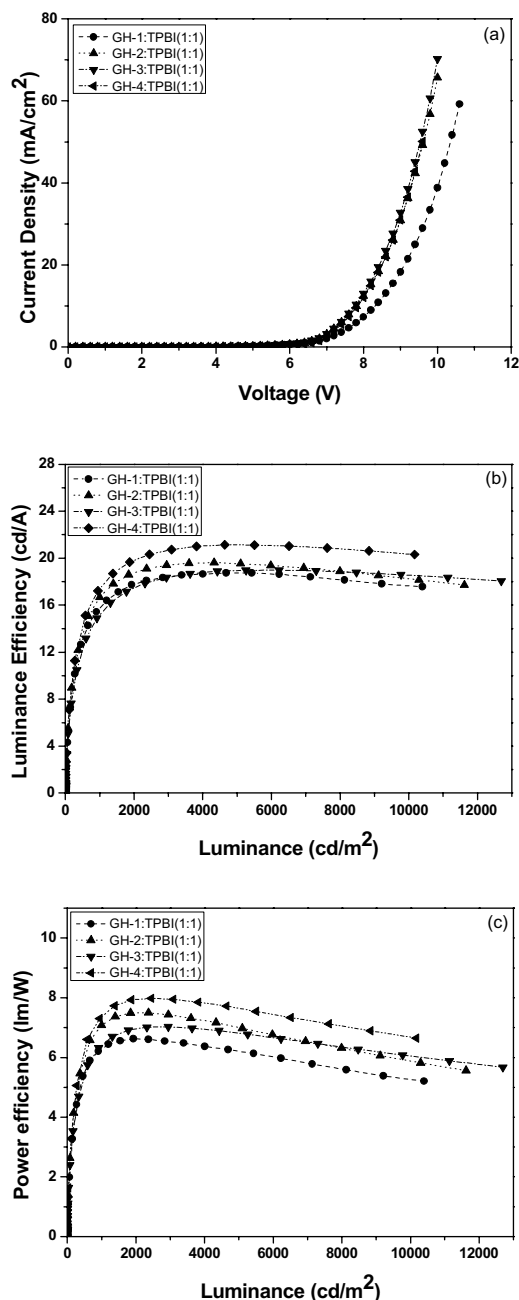
a Maximal brightness.

b Maximal luminous efficiency.

c Maximal power efficiency.

Figure 5 shows the current-voltage and efficiency – brightness characteristics of the devices. All of the EL devices exhibited turn-on voltages in the range of 4.8–5.0 V. GH-4 exhibited the best performance with a maximum current efficiency and power efficiency of 21.1 cd/A and 7.9 lm/W. Efficiency roll-off at higher currents, which is typical in phosphorescent OLEDs, is also observed here. The reason is usually attributed to the triplet-triplet annihilation [7]. Nevertheless, at a high brightness of 8000 cd/m<sup>2</sup>, efficiencies above 18.1 cd/A, 18.8 cd/A, 18.8 cd/A, 20.8 cd/A and 5.6 lm/W, 6.3 lm/W, 6.4 lm/W, 7.0 lm/W, respectively, can be still obtained. For all devices, the EL spectra are seen to be entirely due to green emission with Commission

Internationale de L'Eclairage Chromaticity (CIE) coordinates of 0.31, 0.61 at 1000 cd/m<sup>2</sup>.



**Fig. 5. (a) I-V characteristics of devices, (b) Luminance efficiencies as a function of luminance, (c) Power efficiencies as a function of luminance.**

#### 4. Summary

A series of novel butterfly-shaped host molecules with nonconjugated linkage of carbazole and fluorene moieties has been synthesized and characterized. Green soluble electrophosphorescent devices using

such host materials with TPBI as a co-host show high luminance efficiency and power efficiency. In addition, we achieved very low roll-off efficiency with increasing current density in PhOLEDs, in which the electron transporting TPBI is used as a co-host.

#### 5. References

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