Thermally Stable Hole-Transporting Material for Organic Light-Emitting Diode: an Isoindole Derivative

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A new hole-transporting material, 1,3,4,5,6,7-hexaphenyl-2-{3′-(9-ethylcarbazolyl)}-isoindole (HPCzI), has been synthesized. The new compound is a highly phenylated isoindole with good thermal and chemical stabilities. Thermal analysis using scanning calorimetry shows the compound to have a high melting point at 311.5 °C. Its bulky structure leads to good film-forming properties of the compound via thermal evaporation. Aside from the high hole mobility, the compound possesses other important attributes required for a good hole-transporting host material for applications in organic electroluminescence. The photophysical property of HPCzI and its performance as a hole-transporting material in a double-layered electroluminescent device were investigated. At a drive voltage of 8.8 V and a current density of 20 mA/cm^2, the device with a configuration of ITO/HPCzI/AlQ$_3$/MgAg (30 Ω/□:700 Å:700 Å:2000 Å) showed a green AlQ$_3$ emission with a current efficiency of 3.5 cd/A.

Introduction

Electroluminescent (EL) devices based on organic small molecules and conjugated polymers are a new and exciting form of emissive display technology which holds great potential for flat-panel display applications.[1] Despite the intensive interest and research work, some important and fundamental challenges still remain. For example, there are still needs for improving the operation stability,[2−3] energy efficiency,[4] and color purity[5] of these EL devices, etc. In particular, the high-temperature (e.g., around 100 °C) operational stability of the current organic light-emitting devices (OLEDs) is far from satisfactory.

The thermal instability of organic materials is considered as a major cause of the poor high-temperature operation stability.[6] For example, the widely used hole-transporting materials (HTM) such as 4,4′-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl (NPB) and *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), have rather low glass transition temperatures, T_g, of 95 and 65 °C respectively.[6,7] On the other hand, tris(8-quinolinolato) aluminum (AlQ$_3$), the widely used electron-transporting material, has a much higher T_g of 170 °C.[7] The low T_g of the HTMs suggests that their thin films can be physically transformed much more easily upon operation at high temperatures or high power density. It is thus desirable to develop HTMs of better thermal stability. Isoindole derivatives have been synthesized by the reaction of phthalaldehyde and an amine in the presence of an alkylthiol which was used as the detection method for amino acids, peptides, and proteins.[8] It is also found that isoindole derivatives are highly fluorescent, emitting in blue. Some highly fluorescent polymers containing the isoindole moiety have been prepared and shown to have high glass transition temperatures and high thermal stabilities.[9] In the present work, we report the development of a new HTM with better thermal stability based on a highly phenylated isoindole.

Experimental Section

1. Materials Synthesis. Figure 1 shows the synthetic scheme of a newly designed compound, 1,3,4,5,6,7-hexaphenyl-2-{3′-(9-ethylcarbazolyl)}-isoindole (HPCzI), in four reaction steps. The former three-step precursors, 1,2-bis(benzoyl)-1,2-dibromoethylene, 1,2-bis(benzoly)acetylene, and 1,2-bis(benzoyl)-3,4,5,6-tetraphenylbenzene, can be synthesized by the reported method[10] with high yields of 78.4, 85, and 65%, respectively. In detail, synthesis of HPCzI was carried out following the procedures of a similar reaction described in the literature, as follows.[11]

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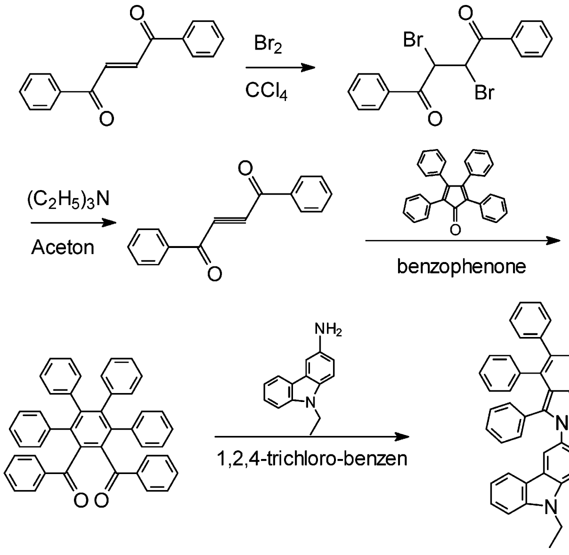

Figure 1. Synthetic scheme of the compound 1,3,4,5,6,7-hexaphenyl-2-{3′-(9-ethylcarbazolyl)}-isoindole (HPCzI).

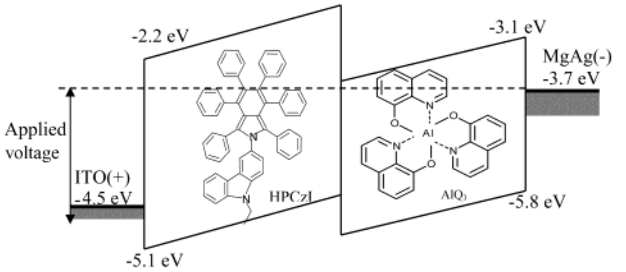

Figure 2. Structure and energy scheme of the device, together with the chemical structures of the organic materials used.

A 50-mL three-neck flask equipped with a N_2 inlet, a condenser, and a magnetic stirrer was charged with 1,2-bisbenzoyl-3,4,5,6-tetraphenylbenzene ($C_{44}H_{30}O_2$, 590.72, 1 g, 1.69 mmol), 3-amino-9-ethylcarbazole (90%, $C_{14}H_{14}N_2$, 1.19 g, 5.08 mmol), 1,2,4-trichlorobenzene (15 mL, bp 214 °C), and *p*-toluenesulfonic acid monohydrate (0.1 g, 0.51 mmol). The mixture was kept at 200 °C for 2 h, and then the resulting dark black solution was cooled to room temperature and 50 mL of methanol was added. The solid precipitate was filtered and washed with 20 mL of methanol 3×. The yellow solid was then recrystallized from toluene 2× to give 0.6 g of 1,3,4,5,6,7-hexaphenyl-2-{3′-(9-ethylcarbazolyl)}-isoindole (46.2% yield): mp 311.5 °C. ^{1}H NMR (300 MHz, in $CDCl_3$, δ (ppm)): 1.33 (t, 3H, $-CH_3$), 4.21 (q, 2H, $-CH_2-$), 6.54−7.60 (m, 36H), 7.79 (d, 1H). Calculated for $C_{58}H_{42}N_2$: C, 90.82; H, 5.47; N, 3.65. Found: C, 90.84; H, 5.43; N, 3.63.

The photoluminescence (PL) and absorption spectra of HPCzI were measured, respectively, with a Perkin-Elmer LS50 fluorescence spectrophotometer and a Perkin-Elmer Lambda 2S UV−Visible spectrophotometer.

2. Electronic Characterization. The ionization potentials (IPs) of materials used in device fabrication were determined by ultraviolet photoelectron spectroscopy (UPS) using the samples prepared by vacuum deposition on ITO substrates, and the energy levels of lowest unoccupied orbital (LUMO) were approximately defined as differences between IPs and long-wavelength cutoffs of the absorption spectra of thin films on quartz substrate.

3. Device Fabrication. The structure and the chemical structures of the organic materials used in the present device are shown in Figure 2. Devices were fabricated with a configuration of glass/indium-tin-oxide (ITO)/HPCzI/AlQ$_3$/MgAg (30 Ω/□: 700 Å :700 Å: 2000 Å; mass ratio of Mg/Ag is 10:1). The ITO glass substrate was cleaned with detergent and deionized water, and dried in an oven for about 2 h. The substrate was then treated with UV−Ozone for 25 min before it was loaded into a deposition chamber with a base pressure of 5×10^{-7} Pa. The organic films and metal electrode were sequentially deposited on the substrate by thermal evaporation. The deposition rates were 2−3 Å/s for the organic materials and 5−7 Å/s for the cathode metals. The current−voltage−luminance characteristics and EL spectra were measured with a computer-controlled direct-current power supply and a Spectrascan PR650 photometer at room temperature. The emission area of the devices is 0.1 cm^2, as defined by the overlapping area of the anode and cathode.

Results and Discussion

As depicted in Figure 1, the synthetic procedure of HPCzI involved four steps using low-cost starting materials. Also, the first three steps could be carried out easily with high yields. However, more efforts were needed in the final step, which involved the use of catalyst under inert atmosphere at high temperatures. So far, a yield of only 46% was achieved. Nevertheless, the resulting highly phenylated isoindole, HPCzI, is very stable in air and has a high melting point of 311.5 °C. The isoindole moiety of HPCzI is surrounded by six phenyl rings and an *N*-ethylcarbozole. This bulky structure of the compound renders the reaction with other reagents difficult by sterically hindering the access of active species. Generally, bulky molecules will tend to form good films. Both the isoindole and carbozole moieties in HPCzI are electron rich and function as electron-donating groups because of the lone-pair electrons in the sp^3 nitrogen atoms. The presence of an electron-donating group is known to contribute to the hole-transporting property of a molecule.[12] So, it is reasonable to expect HPCzI to have good hole-transporting property. In addition, a good HTM should have the following characteristics: (1) high thermal stability; (2) small hole-injection barrier at its interface with the anode; and (3) good film-forming properties. As mentioned above, HPCzI is expected to have the merits of (1) and (3). The ionization potentials (IP) of HPCzI and work function of ITO were measured with ultraviolet photoelectron spectroscopy to be of 5.1 and 4.5 eV, respectively. These IP values suggest a small energy barrier of 0.6 eV as shown in Figure 2, which is slightly smaller than that between ITO and NPB (0.7 eV).

Figure 3 shows the absorption and the PL spectra of HPCzI in dilute solution in different solvents as well as the corresponding spectra measured from a HPCzI film deposited on a quartz substrate. Results are summarized in Table 1. The absorption peaks of HPCzI in different solvents are almost the same, with peaks at 350−370 and 290 nm. This suggests that the polarity of solvent has little influence on the energy levels of HPCzI ground-state molecules. However, the emission peaks of HPCzI in different solvents show clear differences. The emission of HPCzI peaks at 444 nm in *n*-heptane (nonpolar), 455 nm in MeOH (polar proton solvent), and 462 nm in CH_2Cl_2 (medium polarity) and CH_3CN (a strongly polar aproton solvent). The peak shift can be attributed to the stronger interaction between the solvents and the excited molecules. The excited states of HPCzI are more stabilized in polar

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Table 1. Photophysical Data for Compound HPCzI in Different Solvents and in Solid State

source	UV–Vis absorption (λmax/nm (ϵ/ M^{-1}cm^{-1}))			photoemission		
				λ_{em}/nm	fwhm/nm	Φ_{pl} (%)
in *n*-heptane[a]	379 (15960)	351 (14880)	292 (71710)	444.4	61	0.31
in CH_2Cl_2[a]	374 (13290)	352 (14090)	291 (55330)	462.9	64	0.37
in CH_3CN[a]	372 (12800)	351 (14170)	284 (51660)	461.6	64	0.31
in MeOH[a]	374	347	289	455.2	64	0.63
thin film[b]	340–380	300	240	440.0	55	

[a] Compound HPCzI in different solvents. For HPCzI in MeOH, due to the insolubility, the values of ordinate for absorption were too small (less than 0.03) to be used for accurate ϵ (M^{-1}cm^{-1}) calculation. [b] HPCzI thin film with a thickness of 80 Å on quartz substrate prepared by vacuum deposition. The extinction coefficients ϵ (M^{-1}cm^{-1}) and the photoluminescence quantum yield Φ_{pl} for HPCzI film are unavailable.

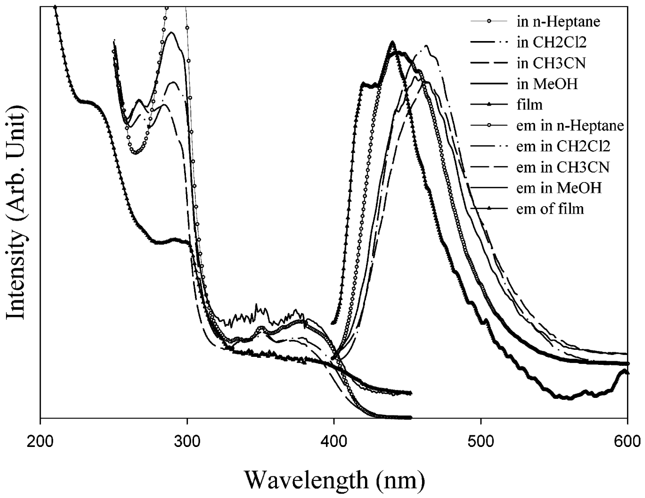

Figure 3. Absorption and photoluminescence spectra from dilute solutions of HPCzI in different solvents and from the HPCzI film. (The excitation wavelength for the photoluminescence spectra is 380 nm.)

solvents than in nonpolar solvents. This leads to a red shift of emission with increasing solvent polarity. It can also be seen from Figure 3 that the PL peak of the HPCzI film is close to that of HPCzI in nonpolar solvent (e.g., *n*-heptane). This means that there is little or no influence of molecular interaction on the excited state of HPCzI molecules in the solid state. This is understandable as the bulky molecular structure of HPCzI can efficiently prevent the close stacking of molecules, and thus reduce the extent of molecule interaction in the solid state.

The fluorescence quantum yields of HPCzI in different solvents were also obtained using quinine sulfate in 1 M sulfuric acid as the standard (fluorescence quantum yield of 0.546).[13] The fluorescence quantum yields in aproton solvents have values ranging from 0.31 to 0.37, whereas the fluorescence quantum yield in proton solvent (methanol) is 0.63. It can be interpreted that special interaction such as hydrogen bonding may play a role in protonic solvents. In short, the spectral and photophysical properties of HPCzI are not sensitive to the environment. This feature is beneficial for OLED applications.

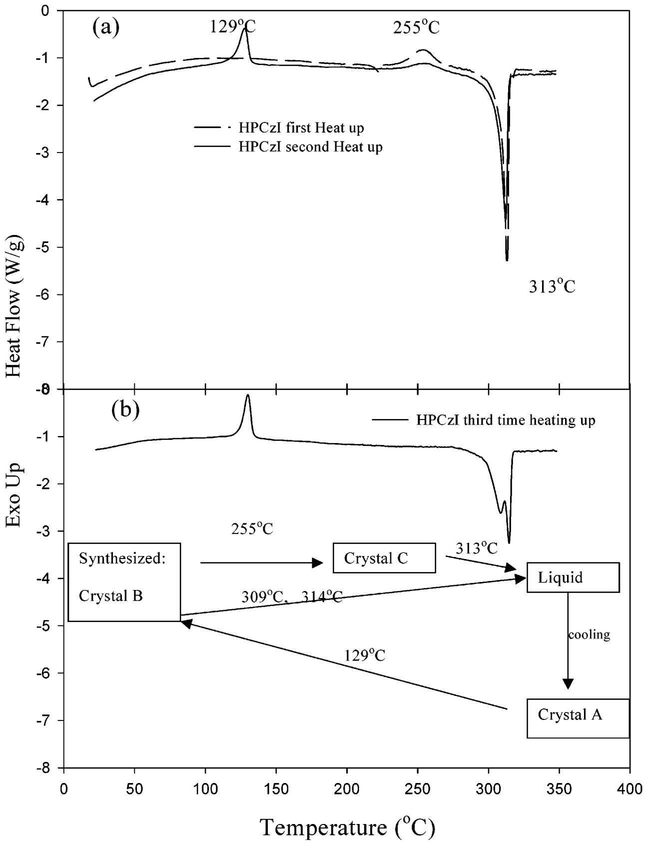

Figure 4. Thermal analysis results of HPCzI using differential scanning calorimetry.

The hole mobility of HPCzI thin film was studied by using transient electroluminescence[14] and compared with NPB, a state-of-the-art HTM. With the applied electric field in the range of 7.6 × 10^5 to 1.4 × 10^6 V/cm, the hole mobility of HPCzI (4.3 × 10^{-5} to 6.0 × 10^{-5} cm^{2}V^{-1}s^{-1} is of the same order of magnitude as that of NPB (7.8 × 10^{-5} to 9.9 × 10^{-5} cm^{2}V^{-1}s^{-1}).

The thermal stability of HPCzI was investigated by using a differential scanning calorimeter (DSC). First, the purified HPCzI compound was heated at a rate of 5 °C/min and the heating curve was recorded, then the sample was cooled to room temperature at a rate of 20 °C/min. Heat flow measurements during the heating and cooling processes were repeated two more times for the same sample. Figure 4a and b, respectively, show the heat flow during the first two and the third heating processes. A schematic summarizing the transformations is also shown in Figure 4b. It can be seen that the synthesized HPCzI (crystallized from solvent) in the state of crystal B was changed to crystal C at 255 °C and then melted at 313 °C. However, after crystallization from liquid another crystal form was obtained (crystal A). Upon the second heating process, crystal A changed to crystal B at 129 °C and changed to crystal C at 255 °C, and then melted at 313 °C.

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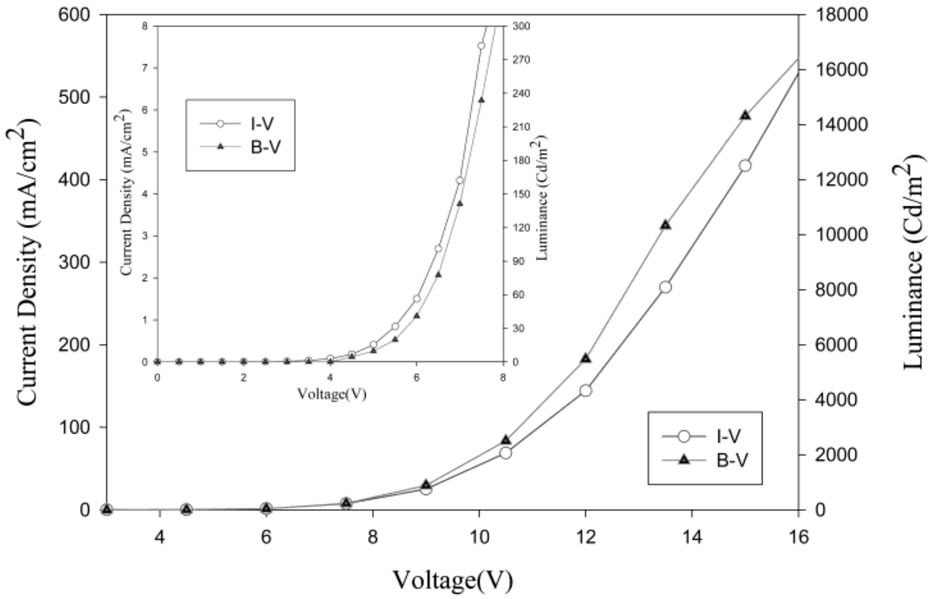

Figure 5. B−I−V chacteristics of a device with the configuration of ITO/HPCzI/AlQ$_3$/MgAg (30 Ω/□:700 Å:700 Å:(10:1) 2000 Å).

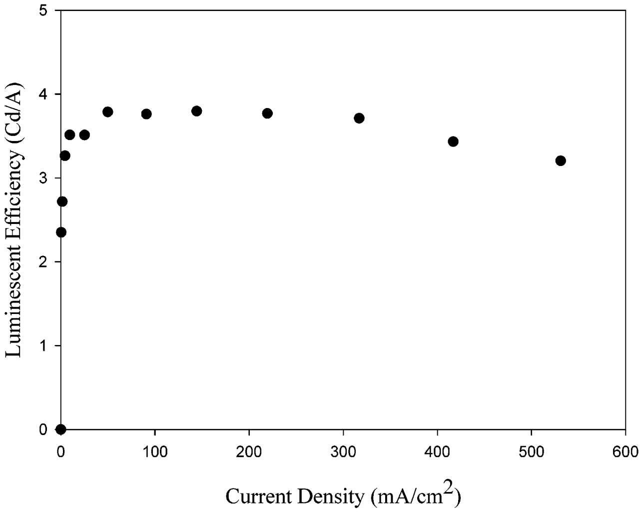

Figure 6. Luminescence efficiency of the device as a function of current density.

Some difference appeared in the third heating process. Crystal B did not change to crystal C, but gave two melting peaks at 309 and 314 °C. This suggests that there may be more than one crystalline phase in crystal B with slightly different melting points. The reason for the disappearance of the transition from crystal B to crystal C is not yet clear. Unfortunately, the glass transition temperature of HPCzI could not be found in our DSC experiments because we could not obtain an amorphous phase of HPCzI even by cooling the melt at a rate of 200 °C/min. Nevertheless, the DSC results show that HPCzI is relatively thermally stable and has the coexistence of multi-conformers. These multi-conformers can increase the tendency to form amorphous film, which is desirable for OLED fabrication by thermal evaporation.[15] It has been reported[16] that the ratio of the melting temperature (mp) to T_g for most molecules is between 1.5 and 2.0. Using this rule of thumb, we deduce the T_g of HPCzI (mp 311.5 °C) to be around 150 °C.

To evaluate the performance of HPCzI as a HTM in OLED, a double-layer device with the configuration of ITO/HPCzI/AlQ$_3$/MgAg (30 Ω/□:700 Å:700 Å:10:1, 2000 Å) was fabricated. In the device, HPCzI serves as a HTM and AlQ$_3$ serves as both the electron transporting and emitting material. The device emits the green color of AlQ$_3$ (532 nm) but no emission from either the HPCzI or any exciplex was observed. This indicates that in the current device HPCzI only plays the role of a HTM.

Figures 5 and 6, respectively, show the I−V−B characteristics and the current efficiency of the device. As can be seen from the inset of Figure 5, the double-layer device exhibits a low turn-on voltage (defined as the voltage need to deliver a brightness of 1 cd/m^2) of 3.8 V, which is partly attributed to the low energy barrier (0.6 eV) between anode (ITO) and HPCzI.[17] At a current density of 20 mA/cm^2 and a drive voltage of 8.8 V, the device showed a current efficiency of 3.5 cd/A and a power efficiency of 1.25 lm/W. The emission spectrum peaks at 532 nm and is independent of the luminance (or current). These values are better than the corresponding ones of the prototypical NPB/AlQ$_3$ device reported by Van Slyke et al.[18] and comparable with the best NPB/AlQ$_3$ device we made using the same equipment, device structure, materials, and fabrication process. It is also worth mentioning that the current efficiency of the present device decreases very slowly with increasing current density (Figure 6). This is definitely beneficial for applications requiring high excitation density such as for passive matrix displays.

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