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Efficient blue electroluminescent device using tetra(β-naphthyl)silane as a hole-blocking material

Gui Yu,[a] Xinjun Xu, Yunqi Liu,[a),b)] Zuoquan Jiang, Shiwei Yin,
Zhigang Shuai, and Daoben Zhu[a]
Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Xiaobang Duan and Ping Lu
Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

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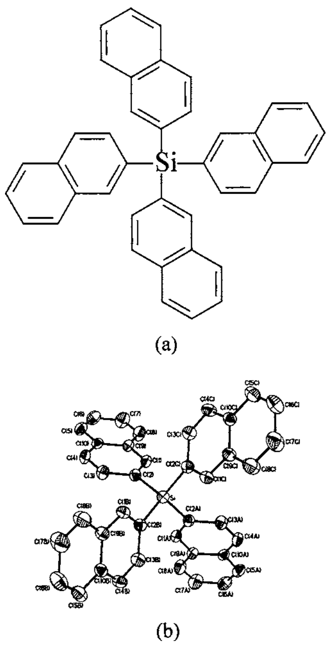
We report an efficient blue light-emitting diode (LED) using *N*, *N*′-bis(1-naphthyl)-*N*, *N*′-diphenylbenzidine as an emitting layer and tetra(β-naphthyl)silane (TNS) as a hole-blocking layer (HBL). We find that the hole-blocking performance, thermal stability, and film-forming ability of TNS are improved over those of the prototypical hole-blocking material 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP). The device that used TNS as the HBL exhibits a narrower light emission and higher current efficiency (2.5 cd/A) as compared with the device containing BCP as the HBL. TNS should be promising as an excellent hole-blocking layer in LEDs. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2138812]

Organic electroluminescent devices have recently attracted much interest because of their potential applications in large-area flat panel displays and light sources.[1,2] To achieve optimum device performance, it is desirable to have multilayer structures that contain discrete hole-transport, emissive, hole-blocking, and electron-transport layers (HTLs, EL, HBLs, and ETLs, respectively). In the past decades, much progress has been focused on improving the properties of organic charge-carrier transport and emissive materials.[3–10] However, until now, there are still many challenges in achieving a high-resolution full color display. One of the most important problems is the lack of excellent hole-blocking materials. The function of the HBL is to block hole overflow from, and confine excitons within, the EML. The use of the HBL is essential to confine the emissive area and to obtain high-efficiency phosphorescent and blue fluorescent LEDs. The hole-blocking materials must have these characteristics: large energy gap, high ionization potential, no emission from the hole-blocking materials, and no interaction either between the emissive materials and the hole-blocking ones or between the hole-blocking materials and the electron-transport ones. Although 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), triazole (TAZ), and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) have been revealed to be very effective hole-blocking materials with relatively high ionization potentials,[11–13] the number of hole-blocking materials available for a high-efficiency emitter is still limited. The major drawback of PBD is the low glass-transition temperature (T_g) and that it is easily crystallized from the organic layer under continuous operation or storage. So far, there have been some reports on organic light-emitting diodes (OLEDs) using TAZ derivatives as an ETL or HBL.[14] However, some organic compounds form exciplexes or charge-transfer (CT) complexes with an adjacent TAZ layer, demonstrating that the triazine core has strong electron-accepting characteristics. In this work, we fabricated an efficient blue OLED using *N*, *N*′-diphenyl-*N*,*N*′-bis(1-naphenyl)-1,1′-biphenyl-4, 4′-diamine (NPB) as an EL and tetra(β-naphthyl)silane (TNS) with an ultrahigh energy gap of 4.0 eV as a HBL. The hole-blocking properties of TNS were assessed. The results indicate that TNS affords more excellent hole-blocking performance, more outstanding thermal stability, and better film-forming ability compared with those of BCP.

The synthesis of TNS was previously described,[15] and its chemical and crystal structures are shown in Fig. 1. TNS crystallized from ethanol is in the tetragonal space group *P* -42(1)*c*. It is found that TNS molecule proves a highly non-co-planar structure with a rigid tetrahedral molecular skeleton, while the conformer of TNS is highly twisted due to the torsion of naphthyl groups above the connecting C-Si bonds.



(a)

(b)

FIG. 1. The (a) chemical and (b) crystal structures of TNS.

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[a] Authors to whom correspondence should be addressed.

[b] Electronic mail: liuyq@mail.iccas.ac.cn

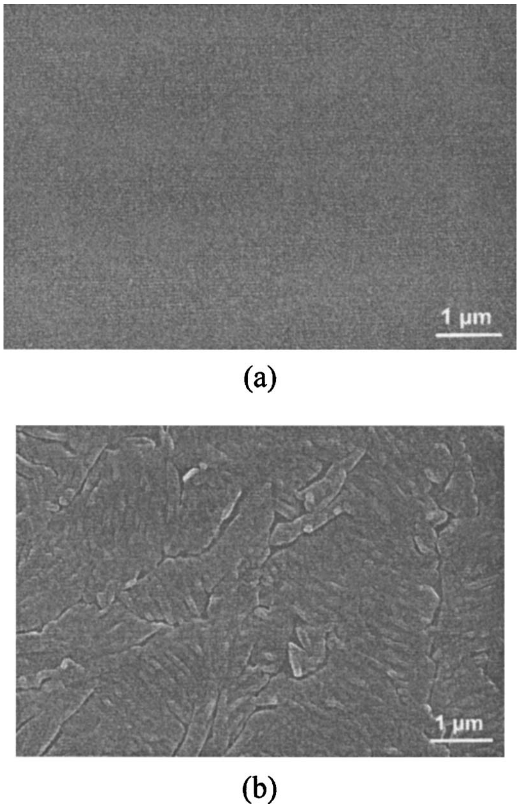

FIG. 2. SEM image of the (a) TNS and (b) BCP thin films on ITO-coated glass substrates.

NPB and BCP (purchased from Aldrich Chemical Co.) were purified by a train sublimation method. The organic EL devices were fabricated on a glass substrate coated with ITO (sheet resistance 30 Ω/□) using a conventional vacuum vapor deposition in a vacuum of 2×10^{-4} Pa. The emitting area of the EL devices was 4 mm^2. The organic layers were grown by means of conventional vacuum deposition. Finally, a thin layer of electron injection-facilitating LiF was introduced, followed by the deposition of 200 nm aluminum as the cathode. A quartz-crystal oscillator placed near the substrate was used to measure the thickness of the thin films, which were calibrated *ex situ* using an Ambios Technology XP-2 surface profilometer. The absorption and photoluminescence spectra were recorded with a General TU-1201 UV-vis spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4300 scanning electron microscopy. Brightness and chromaticity coordinates were measured with a Photo Research 650 Spectrascan colorimeter. Current–voltage $(I-V)$ characteristics were measured with a Hewlett-Packard 4140B semiconductor parameter analyzer. All the measurements were performed under ambient atmosphere at room temperature.

An excellent hole-blocking material should have a high thermal stability and an outstanding film-forming ability. Tetraphenylsilane derivatives, diphenyldi(*o*-tolyl)silane (DPDTSi), *p*-bis(triphenylsilyl)benzene (*p*-BTPSiB), *m*-bis(triphenylsilyl)benzene (*m*-BTPSiB), 9,9′-spirobisilaanthracene (SBSA), and 5,5′-spirobi(dibenzosilole) $[Si(bph)_2]$ with ultrahigh energy gaps were employed as host materials in deep blue electrophosphorescent devices, whereas they exhibit low T_g ranging from 26 to 53 °C (Refs. 16,17). Their low T_g and poor film-forming ability will confine themselves to be used in LEDs. TNS shows a good thermal stability with a thermal decomposition temperature (T_d) at 463 °C, which is higher than that of BCP (T_d=365 °C), demonstrated by thermogravimetric analysis (TGA). Simultaneously, TNS exhibits a higher T_g (73°C) than those of the above five tetraphenylsilane derivatives.[16,17] Figure 2 shows a SEM image of the TNS thin film on an indium-tin-oxide (ITO)-coated glass substrate. TNS has excellent film-forming ability, which offers a smooth and flat thin film without any pinholes by thermal evaporation. This fact results from the three-dimensional nonplanar structure and the weak intermolecular interaction in the solid state according to the crystal structure. For comparison, the same experiments were conducted with a BCP film. Upon deposition, a quite rough surface and many small crystals were observed on the BCP layer. It is evident that the thermal stability and film-forming ability of TNS are improved over those of BCP. Therefore, TNS can be an effective candidate for hole-blocking materials used in organic LEDs.

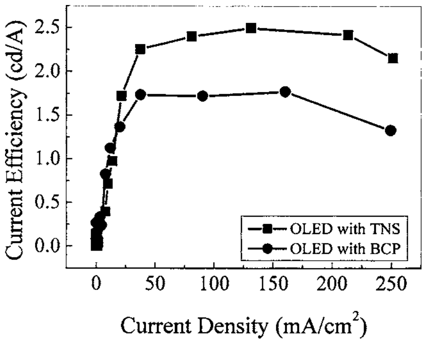

FIG. 3. Current density-current efficiency characteristics of the devices ITO/NPB/TNS/Alq_3/LiF/Al and ITO/NPB/BCP/Alq_3/LiF/Al.

Table I summarizes the physical characteristics of the TNS and BCP thin films. The absorbance and emission maxima of the TNS thin film are noted at 283 and 376 nm, which are blueshifted compared to that of BCP (282 and 403 nm).[18] The optical energy gap (4 eV) for TNS is larger than that of BCP (3.6 eV). From these results, we expect that TNS should be used as a hole-blocking material. Two multilayer organic LEDs using either TNS or BCP as a hole-blocking layer and NPB as an emitting layer were fabricated and their characteristics were compared. The BCP device was used as a benchmark for comparison purpose only. In order to obtain high-efficiency blue LEDs, NPB was employed as the emissive material due to its excellent color coordinate in CIE chromaticity. NPB has a large Stokes shift of 105 nm. A small overlap between the absorption and fluorescent spectra is advantageous in a luminous material. Light emitted from the excited singlet state leaves the film without being absorbed by the remaining molecules. The device has the fol-

TABLE I. Optical properties of TNS and BCP compounds in thin films.

Compound	$\lambda_{max,abs}$ [a] (nm)	$\lambda_{onset,abs}$ [b] (nm)	$\lambda_{max,PL}$ [c] (nm)	Eg [d] (eV)
TNS	283	310	387	4.0
BCP	282	345	403	3.6

[a] Absorption peak.
[b] Absorption onset.
[c] Photoluminescent peak.
[d] Optical energy gap determined from absorption onset.

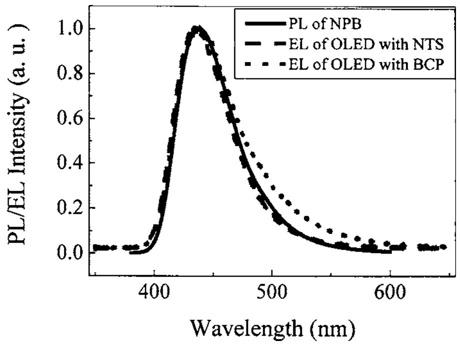

FIG. 4. The PL spectrum of NPB and EL spectra of the devices ITO/NPB/TNS/Alq$_3$/LiF/Al and ITO/NPB/BCP/Alq$_3$/LiF/Al.

lowing structure: ITO/NPB(56 nm)/BCP or TNS(54 nm)/tris(8-hydroquinolate)aluminum(Alq$_3$, 10 nm)/LiF(1 nm)/Al. The forward light output-voltage characteristics for the devices are presented in Fig. 3. It is found that at a similar current density (130 mA/cm^2), both the brightness and current efficiency of the TNS device (3285 cd/m^2 and 2.5 cd/mA) are about 1.5 times higher than those of the BCP device. Figure 4 shows the photoluminescence (PL) spectrum of NPB and the EL spectra of the above LEDs. The EL spectrum of the device containing the TNS layer exhibits the shape and the emission maximum at 437 nm similar to the PL spectrum of NPB, indicating that the emission comes solely from the NPB. It is found that the EL spectrum of the BCP device also shows an emission peak at 437 nm, but an appreciable emission enhancement at the long-wavelength region is observed. This phenomenon may result from the main emission of NPB accompanied by the weak emission of Alq$_3$. Kijima and co-workers obtained a similar result for the device using NPB and BCP as the emitting layer and the hole-blocking layer, respectively.[11] The above results indicate that TNS appears to have a better hole-blocking ability than that of the well-established hole-blocking material, BCP.

The difference in performance between the TNS and BCP devices can be rationalized by comparing the relative highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbit (LUMO) energies. Density-functional calculations to calculate energy levels for the TNS and BCP molecules were performed with the Hartree-Fock 6–31G(5*d*) level of theory using the GAUSSIAN 98 program. Both the HOMO (−7.65 eV) and the LUMO (−2.14 eV) energies of the TNS molecule are lower than those of BCP (HOMO: −7.54 eV, LUMO: −2.3 eV). This result indicates that the energy offset between the HOMOs of TNS and NPB is larger than the one expected between BCP and NPB. Such a large energy offset is expected to lead to an increased barrier for migration of the hole from NPB to HBL and to confine excitons within the NPB layer, thereby all emissions originate from NPB. This results in excellent color purity and a relatively narrow spectrum for the TNS device.

In conclusion, we demonstrate that TNS could be used as an excellent hole-blocking layer to fabricate efficient blue light-emitting devices. TNS exhibits higher thermal stability, better film-forming property, and more outstanding hole-blocking ability than those of the most extensively used hole-blocking material BCP. The device using TNS as the hole-blocking layer shows a current efficiency of 2.5 cd/mA, which is 1.5 times higher than that of the BCP device. This study demonstrates a potentiality of replacing BCP with TNS as the hole-blocking materials in OLEDs, paving the way for the development of other new hole-blocking materials. This study also points to an important parameter to consider in designing new materials for high efficiency blue devices.

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