Efficient organic light-emitting diodes with undoped active layers based on silole derivatives

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We report on efficient molecular organic light-emitting diodes (MOLEDs) composed of novel silole derivatives as an electron transporting layer and an emissive layer. The silole derivative, 2,5-bis-(2′,2″-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilacyclopentadiene, used for the electron transport layer exhibits fast electron mobility of 2×10^{-4} $cm^2/V\,s$ at 0.64 MV/cm measured by the time-of-flight technique. Another silole derivative, 1,2-bis(1-methyl-2,3,4,5-tetraphenyl silacyclopentadienyl)ethane, used for an emissive layer exhibits blue-green fluorescence with an absolute quantum yield of $97\pm3\%$ in the solid state. The devices using silole derivatives show a very low operating voltage, an external electroluminescence quantum efficiency (η_{EL}) of 4.8 %, and luminous power efficiency of 9 lm/W at a brightness of 100 cd/m^2. This value of η_{EL} is the best efficiency achieved for MOLED using undoped emissive and carrier transport layers and is close to the theoretical limit for a device using a fluorescent emitter. © *2002 American Institute of Physics.*
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For high-performance organic light-emitting diodes (OLEDs), there are two major issues in material development. Materials which offer better electron injection/transport properties with respect to the type of electrodes or structure used in OLEDs, and very high photoluminescence quantum yield (ϕ_{PL}) in the solid state are highly desirable. For improving electron injection, it has been demonstrated that the insertion of a thin layer of an alkali metal[1] or alkali metal compounds[2,3] between the cathode and the organic layer leads to a significant enhancement in electron injection. Conversely, few organic compounds exhibit high electron mobility in the amorphous solid state.[4–6] In addition, most electron transport materials exhibit dispersive carrier transport, which indicates the presence of multiple electron trapping sites. Recently, we have reported that a silole derivative, 2,5-bis(2′,2″-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenyl silacyclopentadiene (PyPySPyPy), exhibits nondispersive and air-stable electron transport with a high mobility of 2×10^{-4} $cm^2/V\,s$ at $E=0.64$ MV/cm.[7] This mobility is more than two orders of magnitude higher than that of the most widely used electron transport material, tris (8-hydroxyquinolinolato) aluminum (III) (Alq_3), in OLEDs.[8]

For realizing high ϕ_{PL} in solid films, doping of a highly fluorescent or phosphorescent molecule (guest) into the emitting layer (host) has been accepted as the most effective approach. Energy transfer from the host to the guest molecules[9] and/or direct carrier recombination on the guest molecules[10] lead to efficient emission from the guest. Although doping offers high ϕ_{PL} and other advantages such as an improvement of temperature dependence of external electroluminescence (EL) quantum efficiency (η_{EL}),[11] it complicates the fabrication process and may affect production cost. Thus, it would be ideal if one can achieve very high ϕ_{PL} in an undoped solid film.

In this study, we report a detailed study on high-performance MOLEDs based on silole derivatives. One of the silole derivatives, 1,2-bis(1-methyl-2,3,4,5-tetraphenylsilacyclopentadienyl)ethane (2PSP), exhibits a 100% ϕ_{PL} in the vapor deposited solid films. Using these silole derivatives for both electron transport and light emission, we have fabricated devices with a very low operating voltage and a high η_{EL} of 4.8% photon/electron *without doping any of the layers*.[7] This η_{EL} is close to the theoretical limit for a device using a fluorescent emitter.

The chemical structures of the silole derivatives used in this study are shown in Fig. 1. They were synthesized by a one-step process from bis(phenylethynyl)silanes based on the intermolecular reductive cyclization followed by the palladium-catalyzed cross coupling with aryl halide.[12] The crude products of PyPySPyPy and 2PSP were purified by recrystallization, column chromatography, and vacuum sublimation. Elemental analysis was employed for confirming the purities of silole derivatives. Calcd (%) for PyPySPyPy

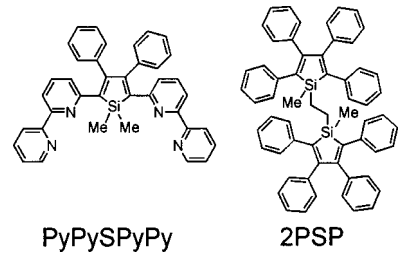

FIG. 1. Chemical structures of the silole derivatives used in this study.

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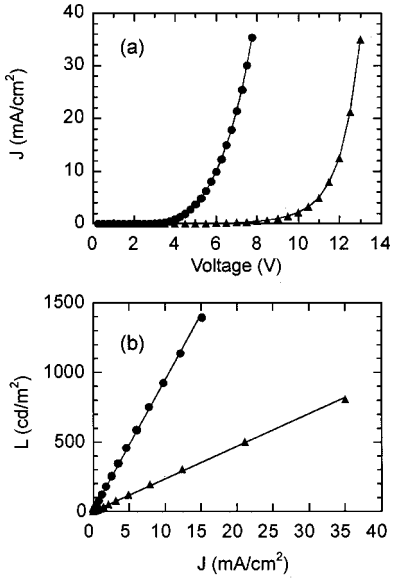

FIG. 2. (a) Current density vs voltage ($J-V$) characteristics and (b) luminance vs current density ($L-J$) for the devices using PyPySPyPy as an electron transport layer and 2PSP as an emitting layer (closed circle), and Alq_3 as an electron transport/emitting layer (closed triangle).

($C_{38}H_{30}N_4Si$): C 79.97, H 5.30, N 9.82; found C 79.80, H 5.26, N 9.59. Calcd (%) for 2PSP ($C_{60}H_{50}Si_2$): C 87.12, H 6.09, found C 87.00, H 6.10. High purity Alq_3 and N,N'-diphenyl- N,N'-bis (3-methylphenyl)-1,1′-biphenyl-4,4′diamine (TPD) were purchased from H. W. Sands Corp. and used without further purification.

Light-emitting diodes were prepared on a glass substrates coated with patterned indium tin oxide (ITO) electrodes. The ITO coated glass substrates (ITO thickness is 100 nm and sheet resistance is about 20 Ω/sq) were precleaned and treated with an oxygen plasma. Devices were prepared by consecutive vapor deposition of a TPD hole transport layer (50 nm), a 2PSP emitting layer (20 nm), and a PyPySPyPy electron transport layer (30 nm). Mg and Ag (10:1 ratio by weight) codeposited through a shadow mask completed the device fabrication. The thickness of the Mg:Ag film is 100 nm. As a reference, a control device with Alq_3 (70 nm) as an electron transporting/emitting layer was fabricated. A quartz crystal microbalance was used to monitor the rate of deposition of all the layers and estimate their thickness.

Current–voltage–luminance measurements of the devices were performed with a Keithley 238 high-current source measurement unit and a Minolta LS-110 luminance meter. The η_{EL} defined as the ratio of the number of photons emitted from the device to the number of injected electrons, was calculated by taking into account both the distribution of photon energy (i.e., EL spectra) and the angular dependence of the EL intensity from the device surface.[13] The angular dependence of the EL intensity was measured with a device mounted on a rotating stage. The ϕ_{PL} of 2PSP films, deposited on silica substrates, was measured using an integrating sphere.[14] All measurements were performed in a glove box filled with a nitrogen atmosphere with <1 ppm oxygen and moisture concentrations.

Figure 2(a) compares current density vs voltage ($J-V$) curves of the devices based on the silole derivatives and

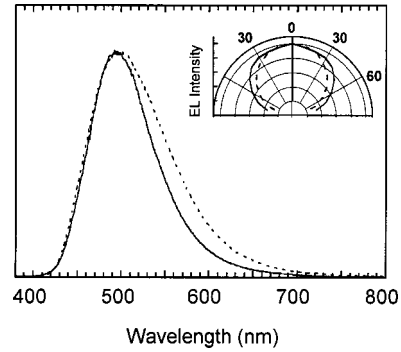

FIG. 3. EL spectra of the devices based on the silole derivatives (solid line) and PL spectra of a 2PSP film used as an emitting layer (dotted line). Inset: The angular dependence of the emission intensity from a device using the silole derivatives. The broken line shows the calculated Lambertian emission pattern.

Alq_3. A significant decrease in the operating voltage was observed in a device based on the silole derivatives. This reduction in voltage can be explained by the higher electron mobility of PyPySPyPy relative to that of Alq_3. High electron mobility of the silole can be attributed to a large electron affinity (E.A.) due to the $\sigma^*-\pi^*$ conjugation in the silole ring and a high aromaticity of its anionic species.[7] A large E.A. is also expected to contribute to the decrease in the operating voltage due to a lowered electron injection barrier.[15] To estimate the electron injection barrier, the ionization potentials of the silole derivatives and Alq_3 were measured by ultraviolet photoemission spectroscopy. By taking into account the shift of the vacuum level at the organic/metal substrate interface, we verified that PyPySPyPy shows a smaller injection barrier for electron injection than that of Alq_3 at the organic/metal interface.[16] Bright blue-green emission ($\lambda=500$ nm) was observed at 2.5 V and a luminance (L) exceeding 1400 cd/m^2 was observed at 6.5 V ($J=15$ mA/cm^2), as shown in Fig. 2(b).

Figure 3 shows that the PL and EL spectra are very similar with a slight decrease in the EL spectrum at longer wavelength. The observed difference between the PL and EL spectral shape can be attributed to an optical interference (or weak microcavity) effect between the ITO anode and the metal cathode. If there was no interference in the device, the emission intensity should follow a Lambertian pattern. We measured angular dependence of the EL intensity as shown in the inset of Fig. 3. The observed deviation from the Lambertian emission pattern supports the presence of an optical interference effect. The emission pattern of the device affects the calculation of total luminance flux.[13] Hence, it is very important to accurately evaluate the device efficiencies based on a corrected emission pattern. A correction factor of 1.2 was used in the calculations of the luminous power efficiency and the η_{EL}. The luminous efficiencies of the device using silole derivatives are 12 lm/W at 10 cd/m^2 ($V=3.25$ V) and 9 lm/W at 100 cd/m^2 ($V=4.0$ V). Even at much higher luminance, the device sustains reasonably high luminous efficiency of 4.3 lm/W ($L=1000$ cd/m^2).

Figure 4 depicts the dependence of η_{EL} on the current density for the two devices. A maximum η_{EL} of 4.8% photon/electron is attained at wide range of current densities between 0.01 and 1 mA/cm^2, and is close to the theoretical

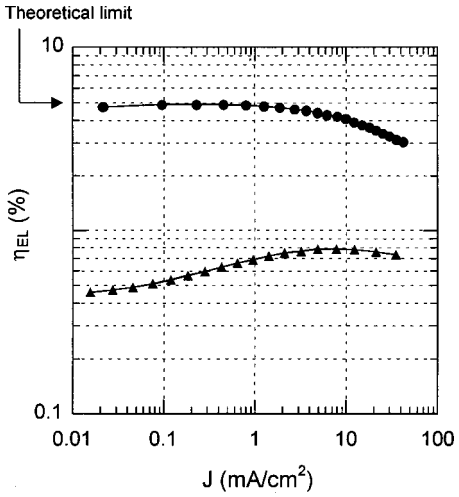

FIG. 4. The external electroluminescence quantum efficiency (η_{EL}) as a function of current density shown for devices using the silole derivatives (closed circle) and Alq_3 (closed triangle). A theoretical limit of $\sim 5\%$ was calculated assuming a refractive index of 1.7 for all organic layers.

limit of $\sim 5\%$[17] for a device using a fluorescent emitter. This result suggests that the device efficiency is primarily limited by two parameters: (i) the fraction of emitted photons that are coupled out of the device ($\sim 20\%$)[18] and (ii) the production efficiency of the singlet excitons imposed by spin statistics ($\sim 25\%$),[19] which suggest that both the carrier recombination efficiency and the ϕ_{PL} of the emitting layer are close to unity. Indeed, we measured an absolute solid state $\phi_{PL} = 97 \pm 3\%$ for the film of 2PSP used as the emitting layer. Such a high ϕ_{PL} is unusual in solid organic films, with few exceptions,[20,21] because of the strong intramolecular interactions. It should be noted that such a high η_{EL} was achieved *without doping* any of the carrier transport and emitting layers. Doping with a highly emissive fluorescent or phosphorescent[22] dyes is a useful and well-known approach for enhancing the ϕ_{PL} of the emitting layer. However, it complicates the fabrication process and requires careful selection of the guest and host molecules in order to maximize energy transfer. Also, doping of the electron/hole transport layers with alkaline metals/Lewis acid is a useful technique for increasing the bulk carrier densities and reducing the carrier injection barrier. However, the effect of the dopant on the device durability is still open to question since ionic impurities result in device degradation.[23]

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