Highly efficient organic light-emitting diodes with a silole-based compound

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Efficient light emission was obtained in a silole-based organic light-emitting diode. A high luminous current efficiency of 20 cd/A, corresponding to an external quantum efficiency of 8%, was achieved. The apparent violation of the upper theoretical limit of 5.5% for the external quantum efficiency of a singlet emitter is discussed. With a suitably designed cathode, a high power efficiency of ~14 lm/W was obtained. A strong dependence of the power efficiency on the thickness of Alq_3 layer is also observed and explained. [DOI: 10.1063/1.1495542]

Much effort has been devoted to increase the emission efficiency of organic light-emitting diodes (OLED). For conventional undoped small-molecule OLED, the highest reported external quantum efficiency (η_{QE}) is ~1.5% in the tris(8-hydroxyquinoline) aluminum (Alq_3)/N, N'-diphenyl-N, N'-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) system.[1] Doping this OLED with phosphors can increase η_{QE} to 7%.[2] Recently, it was found that doping an OLED with triplet emitters could further increase η_{QE} to over 15%.[3] With triplet emitters, luminance power efficiencies (η_P) of over 40 lm/W have been reported. In this letter, we wish to present data showing that, by using 1-methyl-1,2,3,4,5-pentaphenylsilole (MPS) as an emitter, a singlet-emitting OLED without dopants can achieve a high η_{QE} of 8% (equivalent to a luminous current efficiency of 20 cd/A), significantly higher than the 0.65% (Ref. 4) previously reported. With a suitably designed cathode, a high power efficiency of ~14 lm/W has also been obtained.

Theoretically, the overall η_{QE} is a product of the electroluminescence (EL) efficiency of the emitter and the external coupling factor. Assuming a 1:3 singlet–triplet branching ratio, the EL efficiency is limited to 25% for a singlet emitter. Assuming an isotropic source and complete coupling for the cone of light that is not total-internally reflected inside the OLED, the external coupling factor is usually taken to be $\sim 1/(2n^2)$, where n is the refractive index of the emitter. If $n = 1.5$, the external coupling factor is limited to ~22%. Hence, the maximum η_{QE} is ~5.5%. Thus, the present result of 8% efficiency is interesting because it apparently exceeds this theoretical limit. Possible reasons for the high η_{QE} will be discussed.

Siloles or silacyclopentadienes belong to a group of Si-containing conjugated rings with novel molecular structures and unique electronic properties.[5–7] They possess low-lying lowest-unoccupied molecular orbital energy levels associated with the $\sigma^* - \pi^*$ conjugation arising from the interaction between the σ^* orbital of two exocyclic σ-bonds on the ring silicon and the π^* orbital of the butadiene moiety.[7] As a result, siloles can serve as efficient electron-transport materials.[8] A recent study showed that the electron mobility in a silole based compound was ~100 times that of Alq_3, a commonly used electron-transport material.[9] MPS is also a silole-based compound, the chemical structure of which is shown in the inset of Fig. 1.

The OLED devices were fabricated in the usual manner with sequential vacuum evaporation of the various organic layers on 20–30 Ω/□ indium-tin oxide (ITO) coated glass substrates. The ITO glass substrates were cleaned in ultrasonic assisted detergent, followed by rinsing in deionized water before being dried in oven at 100 °C. After 10 min of ultraviolet ozone cleaning, the substrates were transferred into a vacuum chamber for device preparation

TPD was used as the hole-transport layer and MPS as the electron-transport and emission layer. Alq_3 was optionally added as a buffer/electron-transport layer. Both the EL

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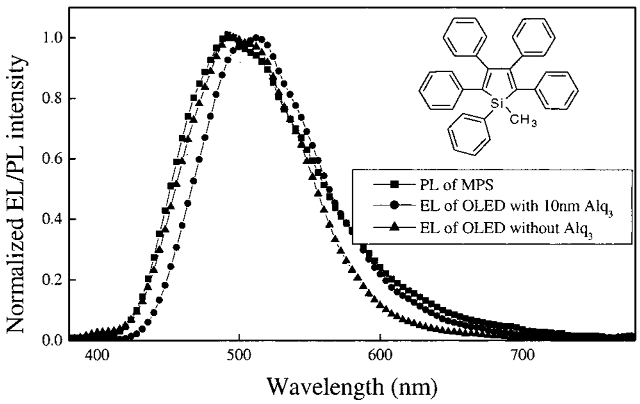

FIG. 1. PL spectrum of MPS and EL spectra MPS-based OLED devices. Shown in the inset is the chemical structure of MPS.

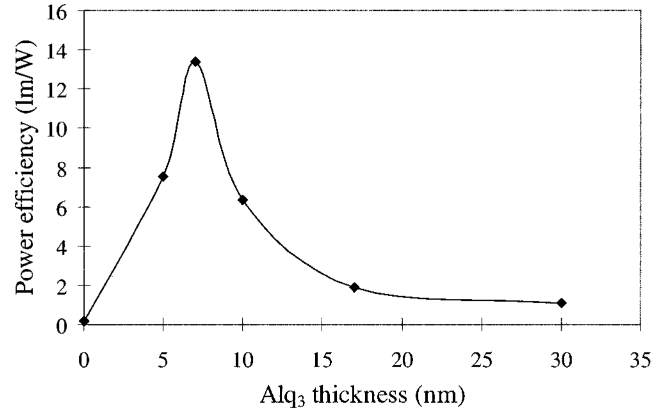

FIG. 2. Dependence of the power efficiency of MPS-based OLED devices on Alq_3 layer thickness.

and photoluminescence (PL) spectra measured using a PR650 photometer were Lambertian. Current (I) and voltage (V) to the device were measured to determine the $I-V$ and luminance (L)-power characteristics, from which the various efficiencies can be calculated. For the cathode, two material configurations were investigated: LiF/Al and Mg/Al. Together with a PL spectrum, the EL spectra of MPS-based OLEDs, with and without an Alq_3 layer, are plotted in Fig. 1. The PL peak of pure MPS lies near 490 nm. For a device containing no Alq_3, the EL and PL spectra are quite similar except for the long-wavelength region beyond 550 nm, where the intensity of the EL spectrum is somewhat weaker than that of the PL spectrum due to the microcavity effect resulting from the presence of the electrodes.[10] As soon as a thin layer of Alq_3 is inserted, the emission peak shifts to 510 nm and there is much less emission on the short-wavelength side. However, the EL spectrum is still quite different from that of Alq_3, implying that emission is still dominated by MPS.

The effects of different cathode designs on the emission efficiency have been examined. It was found that if Alq_3 were not used, Mg/Ag ($\eta_P \sim 4$ lm/W) would be a better cathode than LiF/Al ($\eta_P \sim 0.4$ lm/W). However, the reverse would be true if Alq_3 with a thickness less than $\sim$11 nm were used. In general, devices with Alq_3/LiF/Al as the cathode offered higher efficiencies. In fact, it can be said that the combination of Alq_3/LiF/Al forms a good electron injector for a TPD/MPS OLED.

The thickness of the CuPc, TPD, and Alq_3 layers was systematically varied to optimize the emission efficiency. The most interesting dependence is on the thickness of the Alq_3 layer. Shown in Fig. 2 are the results for a series of samples with the same CuPc/TPD/MPS thickness at 20 nm/50 nm/50 nm. A sharp peak, with $\eta_P \sim 14$ lm/W, is observed at an Alq_3 thickness of 7 nm. Shown in Fig. 3 is the $I-V$ and the L-current density (J) (inset of Fig. 2) characteristics of the 7 nm device, from which η can be obtained at any given J. η_P and η are related by $\eta_P = \pi\eta/V$.

The peak η_P in Fig. 2 is $\sim$14 lm/W. The corresponding η is 20 cd/A. Since both numbers are dependent on the photopic response of the eye, a better indicator is η_{QE}. It can be measured using the PR650, which gives also the photon flux. With a measured Lambertian distribution, η_{QE} is estimated to be $\sim$8% for the 7 nm device. It should be pointed out that these numbers were measured at a low luminance of 5 cd/m^2. At a higher but more representative luminance of 300 cd/m^2, η drops to 16 cd/A, which is still quite large.

Two interesting questions can be asked regarding the data in Fig. 2: (1) Is the high efficiency of the MPS-based OLED device in violation with the known maximum theoretical limit on η_{QE}? (2) What is the physical origin of the sharp dependence of the emission efficiency on the thickness of the Alq_3 layer? To answer the first question, we have to establish that the MPS OLED is indeed a singlet emitter (a triplet emitter, in principle, can have a higher theoretical limit). We also have to measure n of MPS in order to compute the external coupling factor. Using a 3 ns pulsed N_2 laser, the fluorescence decay (Fig. 4) of an MPS thin film was measured. The measured fluorescence lifetime was about 15 ns, with negligible long-decay-time phosphorescence in MPS. This establishes the fact that MPS is predominantly a singlet emitter.

A refractive index of 1.68 at 490 nm (Ref. 11) has also been measured for MPS using spectroscopic ellipsometry. Therefore assuming that the external coupling factor is $1/(2n^2)$ and the singlet:triplet branching ratio is 1:3, the maximum η_{QE} can be calculated to be 4.5%. However, both assumptions have been questioned recently.[12–14] First of all, the $1/(2n^2)$ factor is obtained by assuming an isotropic emission inside the OLED with no interference from the rear

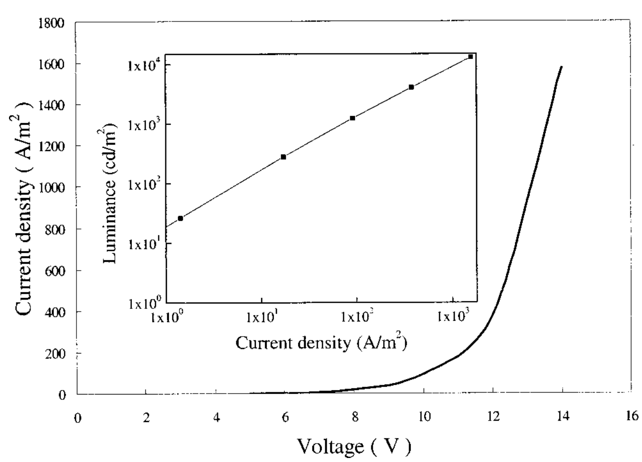

FIG. 3. The $J-V$ characteristics of an OLED device with 7 nm thick Alq_3. Shown in the inset are the $L-J$ characteristics.

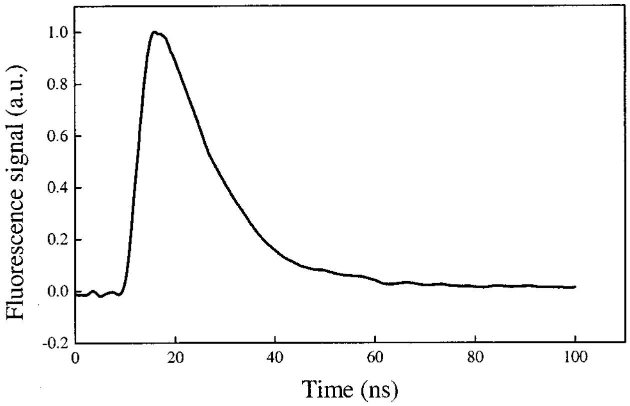

FIG. 4. Fluorescence decay of MPS measured with a 3 ns pulsed N_2 laser.

metal electrode. This assumption is not compatible with a Lambertian radiation pattern. Recently Kim *et al.*[12] pointed out that the emission dipoles were not isotropic but somewhat aligned on the surface of the OLED. Using a model calculation, they showed that the factor should be $0.75/n^2$ to $1.2/n^2$, depending on the alignment conditions of the emitting dipoles. Using an average figure of $1/n^2$, the maximum η_{QE} of the MPS OLED should be ~9%.

Second, there has been some recent debate[13,14] about the singlet–triplet branching ratio. Indeed, the singlet formation cross section is several times larger than the triplet cross section[14] for conjugated polymers. If the branching ratio were greater than 1:3, then the singlet emission quantum efficiency would exceed 25% and η_{QE} could be larger than 9%. Thus, the measured η_{QE} of 8% need not violate the theoretical limit. In fact, the measured 8% value is an indirect evidence supporting the assertion that either coupling factor is greater than $1/(2n^2)$ or the singlet–triplet branching ratio is larger than 1:3.

The strong dependence of emission efficiency on Alq_3 thickness can be explained by the large disparity in electron mobility between MPS and Alq_3. Recently, it has been determined that the electron mobility in silole is ~100 times that of Alq_3.[9] Consequently, the $I-V$ characteristics of TPD/MPS based diodes are particularly sensitive to the thickness of Alq_3, because Alq_3 is much more resistive than either TPD or MPS. In fact, the electron transport in Alq_3 is space-charge limited with J roughly given by[15]

$$J=\left(\frac{9}{8}\right)\varepsilon\mu\frac{V^2}{d^3}, \tag{1}$$

where ε is the dielectric constant, μ is the charge mobility, and d is the thickness of the conducting layer. Since L is proportional to J, it is therefore reasonable to expect a strong decrease of the luminance efficiency as a function of the Alq_3 layer thickness d, as indicated by Eq. (1).

In Fig. 2, the initial increase in efficiency with Alq_3 thickness is due to the need to have some Alq_3 to form a continuous barrier-reducing dipole layer. Since the physical dimension of the dipole layer is small, any excess Alq_3 thickness beyond what is needed will not lead to further reduction in barrier height. It will simply induce an undesirable ohmic drop, increase the turn-on voltage and reduce η_P.

For sure, both detailed transport measurement and rate equation modeling are necessary to fully understand the exciton recombination dynamics in the multilayer device.[16] The most important observation is that MPS is an efficient emitter, though it is not as compatible as Alq_3 is with the LiF/Al cathode. On the other hand, while Alq_3 is compatible with the efficient LiF/Al electron injector, it is not as efficiency an emitter. The present study supports the concept of making an OLED where the emission layer is different from the electron injection layer.

In summary, we have observed highly efficient OLED emission from the material MPS. The measured 8% external quantum efficiency provides indirect evidence that either the singlet:triplet branching ratio or the external coupling factor is larger than the commonly accepted values. Several interesting questions remain before the photophysics of the high external quantum efficiency can be fully explained. In particular, the absolute fluorescence quantum yield and the exact singlet:triplet branching ratio are being carefully studied. The possibility of inducing anisotropic radiation from such molecules is also being investigated. These results will be reported in the future.

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