Surface plasmon-polariton mediated emission from phosphorescent dendrimer light-emitting diodes

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(Received 30 January 2006; accepted 25 February 2006; published online 17 April 2006)

We present experimental results showing electroluminescence from a dendrimer based organic light-emitting diode (OLED) mediated via surface plasmon polariton (SPP) modes. A combination of angle dependent electroluminescence, photoluminescence, and reflectance measurements is used to identify emission originating from the guided modes of the device. It is found that the SPP modes, which are usually nonradiative, are coupled to light by a wavelength scale periodic microstructure. It is demonstrated that the necessary microstructure can be readily fabricated by solvent-assisted micromoulding. Our results indicate that such an approach may offer a means to increase the efficiency of dendrimer based OLEDs. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2193795]

While organic light-emitting diodes (OLEDs) have shown much promise in display applications, their device architecture is such that excitons created within the organic emissive layer may relax via a number of decay routes. These routes may include some or all of the following: surface plasmon-polariton (SPP) modes associated with the metallic cathode/organic interface, waveguided modes within the substrate and organic emissive layers, and Joule heating of the cathode. As a consequence of these decay routes, the intensity of the emitted light from these devices into the far field may be significantly impaired.[1,2] Improving the efficiency with which light is extracted from these structures is thus a key concern.

One class of material that has shown great promise as highly efficient organic emitters are phosphorescent iridium (III) complex cored dendrimers.[3,4] Dendrimers allow fine tuning of photophysical properties by independent variation of core, dendrons and dendrimer generation.[5–7] The combination of high dendrimer light-emitting diode (DLED) efficiency, molecular level engineering of the physical properties, and their suitability for solution processing makes these materials extremely attractive for industrial fabrication processes. However, DLEDs using phosphorescent dendrimer emitters also suffer losses to SPP and waveguided modes, thus diminishing the overall device efficiency.[2] The very high DLED internal quantum efficiency (~80%) of the best dendrimer materials indicates that significant increases in light output from these OLEDs must be sought via increases in the optical outcoupling efficiency of these devices, and it is just such an approach that we pursue here. In particular, we concentrate upon recovering energy lost from the emissive layer to SPP modes as useful light in the far field by modifying the device geometry, an aspect of DLED devices that has not so far been investigated experimentally.

SPPs are guided transverse magnetic (TM) polarized electromagnetic surface modes that occur at the interface between a metal and a dielectric. SPP modes have electromagnetic fields that decay exponentially into both the bounding metal and dielectric media and, as they possess a greater momentum than free space photons of the same frequency, they are nonradiative in nature on a planar interface.[8] Recent calculations have shown that the decay routes by which emissive species may lose power to nonradiative modes depend greatly upon the class of emissive material used. It has been shown that in an OLED containing a conjugated polymer the dominant nonradiative decay channel is via loss to waveguided modes (~35%) while loss to SPP modes is less (~10%).[2] The relatively low loss of power to the SPP modes in conjugated polymer devices arises from the fact that the dipole moment of the conjugated polymer lies predominantly in the plane of the structure.[9] However, in a device containing a dendrimer based emissive material, the dipole moment of the dendrimer may sample all directions in space on a time scale faster than the excited state lifetime and is thus effectively isotropic.[10] For dendrimer based systems the situation is the reverse of that for conjugated polymer devices with the dominant non-radiative decay channel being SPP modes (35%) and waveguide modes being weaker (~10%).[2] In the work presented here it is the power lost to SPP modes that we aim to recover as light in the far field.

The use of wavelength scale microstructure formed by interferometric techniques to scatter nonradiative modes supported by LED devices, thus allowing them to couple to light, has already been demonstrated.[11] These studies have included the recovery of waveguided modes in conjugated polymer devices[12] and SPP mediated emission from small molecule emitters.[13,14] An alternative approach for the formation of periodic microstructured thin films is via solvent assisted micromoulding.[15] Large area gratings with excellent uniformity of depth and profile have been demonstrated in previous studies on conjugated polymers.[16] In the work presented here we have utilized this solvent assisted micromoul-

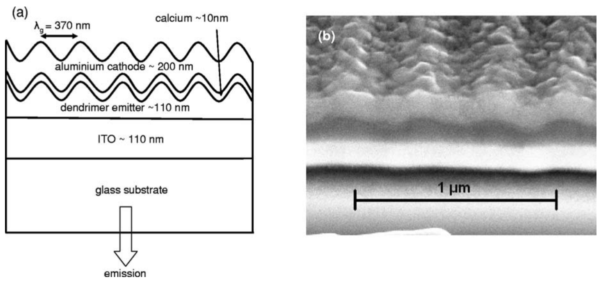

FIG. 1. (a) Schematic representation of the device structure used in our experiment. The layer thicknesses are indicated. (b) SEM image of the experimental device taken at an angle of 52° to the substrate normal.

ding approach to demonstrate, for the first time, SPP mediated electroluminescence (EL) from a dendrimer based OLED.

The experimental device used in this study consisted of a 110 nm thick active layer of 20:80 wt% iridium (III) complex cored dendrimer:CBP blend, spin coated from dichloromethane solution onto a glass-ITO substrate (Merck, 20 $\Omega/\square$). A one dimensional grating of period (λ_g) 370 nm and average depth 50 nm was formed in the active layer by solvent assisted micromoulding, using a siloxane replica grating of a silica master grating that had been fabricated by interferometry. Thermal evaporation of 10 nm of calcium followed by 200 nm of aluminum completed the device by formation of an optically thick cathode. A schematic of the structure is shown in Fig. 1(a), together with a scanning electron microscope image of a portion of the device, Fig. 1(b).

An understanding of the scattering of guided modes from a device can be obtained by measuring the emission or reflectance spectra of a device as a function of angle. The scattered modes appear as additional peaks (emission) or dips (reflectance) in intensity which shift in wavelength as the angle is varied. In the work presented here we use a combination of angle dependent electroluminescence, reflectance, and photoluminescence to identify clearly the mode structure of the experimental device. In order to measure the polarized angle dependent electroluminescence from the device, spectra were taken using an optical fiber connected to a charge-coupled device (CCD) spectrograph with a collection angle of 1°. Rotation of the optical fiber head around the device allowed for collection of the EL emitted through the substrate over a range of polar emission angles θ. The device was driven at 12 V during spectral acquisition, corresponding to a current density of $\sim$4 mA cm^{-2}. Figure 2 shows EL emission spectra measured from the experimental device at an angle normal to the sample surface (θ=0), together with the equivalent emission spectrum from a planar control device, fabricated to the same specification as the experimental device, with the omission of the microstructure. From Fig. 2 a number of distinct EL emission peaks may be seen in the spectra obtained from the microstructured OLED. In comparison with numerical calculations, described below, these peaks have been identified as EL mediated via the SPP mode associated with the cathode/dendrimer-blend interface and transverse electric (TE) and TM waveguided modes associated with the dendrimer-blend and ITO layers.

To determine the modal structure of the OLED, reflectance measurements were taken from the structure over a range of angles of incidence (θ) and wavelengths. When the in-plane wave vector ($k_\parallel$) (in plane being the component in the plane of incidence and parallel to the layers of the structure) of the incident light is equal in magnitude to the sum of the wave vector of the guided mode and the wave vector, of the grating, $k_g=(2\pi/\lambda_g)$, the incident light may couple to the mode. The light within this mode may then reradiate, again upon scattering from the microstructure, and the resulting reflectance spectrum exhibits a characteristic dip in intensity.[17] The reflectance data were converted from incident wavelength and angle of incidence, as measured, to angular frequency and in-plane wave vector and plotted to form an experimentally derived dispersion map. Figure 3(a) shows such a dispersion map constructed from data obtained with TM polarized light incident upon the sample, here dark regions represent areas of low reflectance. A number of reflectance minima may be seen, these features arise when the incident light coupled into modes supported by the structure and then reradiated is π out of phase with the light specularly reflected from the sample.[17] Also shown in Fig. 3(a) is the theoretically derived dispersion of the SPP mode associated with the cathode/dendrimer-blend interface upon scattering by a single grating wave vector. This theoretical dispersion was calculated using Eq. (1), the SPP dispersion relation.[8]

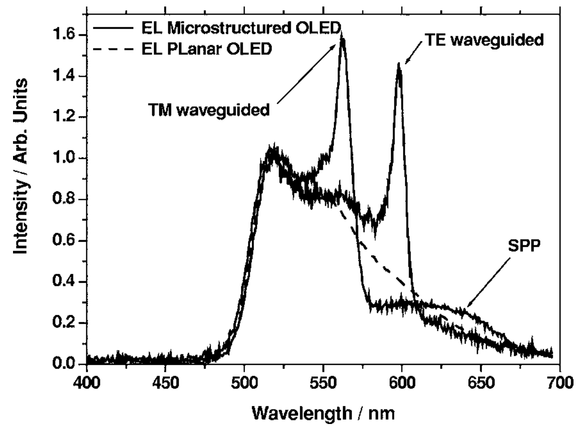

FIG. 2. Representative spectra taken with the polarization perpendicular and parallel to the grating grooves measured at an angle normal to the sample surface (solid lines). The spectra correspond to θ=0° on the TM and TE polarized angular scans, respectively. Electroluminescence spectrum from a planar control device (dashed line).

$$k_{\mathrm{SPP}} = \frac{2\pi}{\lambda_0}\sqrt{\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}}. \qquad (1)$$

Here λ_0 is the wavelength of the light incident upon the sample and ε_1 and ε_2 are the permittivities of both the cathode and the dendrimer-blend emitter, respectively, obtained by spectroscopic ellipsometry. From Fig. 3(a) it can be seen that there is excellent agreement between the theoretically calculated SPP dispersion and the experimentally measured low frequency mode; this and the TM polarized nature of this mode allow us to identify this mode as the cathode/dendrimer-blend SPP. Also, as the theoretically calculated SPP dispersion depends upon the addition/subtraction of a defined grating vector the position of the experimentally measured reflectance minima must be due to an interaction of this mode with the wavelength scale microstructure contained within the device. The higher frequency mode seen in Fig. 3(a) is assigned as a TM polarized waveguided mode associated with the dendrimer-blend/ITO layers.

In order to identify the additional peaks seen in the EL emission features (Fig. 2) EL emission spectra were plotted as a dispersion map, in this case EL emission intensity as a

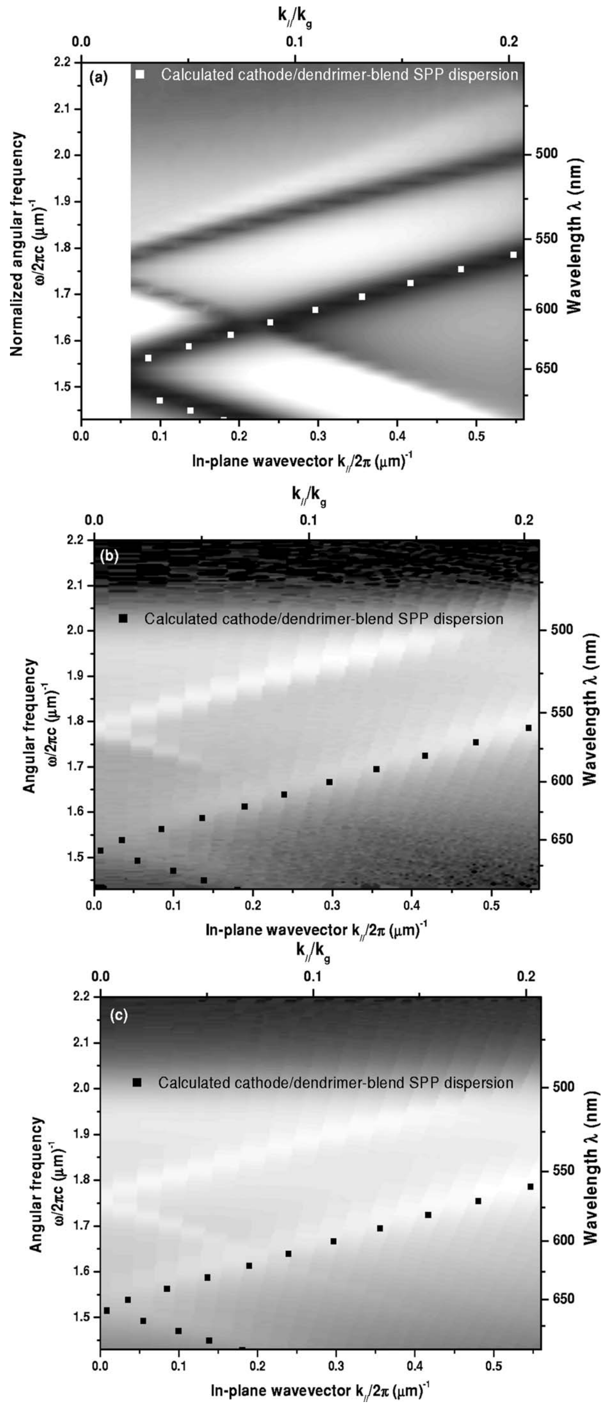

FIG. 3. TM polarized angle dependent luminescence and reflectivity data taken from the experimental device, with the polar angle (θ) in the plane normal to the grating grooves. (a) Reflectance, here dark regions represent low reflectivity. (b) Electroluminescence (EL), light regions represent high EL emission. (c) Photoluminescence (PL), light regions represent high PL emission. Also shown is the theoretically calculated dispersion of the SPP mode associated with the cathode/dendrimer-blend interface. Note that the absence of data in the in-plane wave vector range of 0–0.06 μm^{-1} in Fig. 2(a) is due to the low angle limit of the experimental equipment in measuring reflectance.

function of both in-plane wave vector and angular frequency. Figure 3(b) shows such a dispersion map constructed from TM polarized EL, here white regions correspond to high EL. Comparing these data with those obtained from reflectance measurements, Fig. 3(a), it may be seen that the modes previously identified as the cathode/dendrimer-blend SPP and the TM waveguide modes appear as EL maxima. The appearance of these modes as maxima in the EL data demonstrates that light can be coupled out of SPP modes, which are normally non-radiative, by the addition of an appropriate wavelength scale microstructure. These maxima in the EL emission are shown clearly in Fig. 2 where emission mediated via the SPP mode associated with the cathode/dendrimer-blend interface and the TE and TM waveguided modes may be seen as additional emission peaks when compared to the planar control device.

Finally TM polarized angle dependent photoluminescence (PL) spectra were obtained by optically exciting the dendrimer containing layer with a 410 nm diode laser and collecting the resulting PL emission, again through the substrate.[18] These data are presented in Fig. 3(c) as a dispersion map with white regions corresponding to areas of high PL emission. Comparing these data, Fig. 3(c), with those seen in Figs. 3(a) and 3(b) it may be seen that there is excellent agreement between the reflectance data, EL, and PL data, indicating that experiments using the more accessible optical excitation may be used to infer results about the modal structure of a device that can be expected to be present when the device is electrically excited.

In summary we have demonstrated a working electrically pumped dendrimer based OLED, incorporating a periodic wavelength scale microstructure. We have demonstrated that the microstructure can be made with ease using solvent assisted micromoulding, a simple process that may be suitable for industrial manufacture. The addition of this microstructure has allowed the observation of emission originating from SPP modes and waveguided modes, which are usually trapped within planar devices. This approach has the potential to increase significantly the optical output of OLEDs.

This work has been supported by the EPSRC via the DTI-Link project XTRAOLED.

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