

## Near-infrared electroluminescence of polymer light-emitting diodes doped with a lissamine-sensitized Nd<sup>3+</sup> complex

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We report 890 nm luminescence from a neodymium-doped polymer light-emitting diode. The active layer is a blend of poly(dioctylfluorene-co-benzothiadiazole), F8BT, and a lissamine-functionalized terphenyl-based neodymium complex. We detect electroluminescence from both the lissamine (580 nm) and the Nd<sup>3+</sup> complex (890 nm). By comparison with lissamine-free devices we show that the lissamine is crucial to infrared emission. The neodymium/lissamine luminescence intensity ratio is higher under electrical excitation than under optical excitation, showing that more triplets reach Nd<sup>3+</sup> under electrical excitation. High turn-on voltages provide a clear indication for charge trapping onto the lissamine, and we consider direct triplet formation on the lissamine to be competing efficiently with respect to slower Dexter-type triplet transfer from the F8BT to the lissamine. © 2001 American Institute of Physics. [DOI: 10.1063/1.1359782]

Polymer light-emitting diodes (LEDs) are the focus of much commercial and academic interest owing to the potential for inexpensive fabrication of full-color displays over large areas, and because a number of unresolved issues exist regarding the basic properties of neutral and charged excitations in these disordered carbon-based molecular semiconductors. Although most investigations have focused on electroluminescent devices emitting in the visible spectrum, there is considerable potential to be exploited for emission in the near-infrared and infrared spectral ranges, in particular in connection with optical telecommunication applications. For example, planar optical amplifiers operating at wavelengths of 1.3 or 1.5  $\mu\text{m}$  are essential components of photonic integrated circuits, in which they can compensate for splitting and wave guide losses. Trivalent rare-earth ions like, e.g., neodymium (Nd<sup>3+</sup>) or erbium (Er<sup>3+</sup>), are used as the active element in these planar amplifiers, due to their intra- $4f$  transition at 1340 nm (Nd<sup>3+</sup>,  $^4F_{3/2} \rightarrow ^4I_{11/2}$ ) or 1530 nm (Er<sup>3+</sup>,  $^4I_{13/2} \rightarrow ^4I_{15/2}$ ). These amplifiers typically use inorganic hosts,<sup>1</sup> and are pumped using an external pump laser. Recently, we and others have reported the synthesis of rare-earth doped polymer wave guides.<sup>2,3</sup> Combining this recent work with the knowledge of electrical excitation processes in polymer LEDs, it may become possible to fabricate an electrically pumped optical amplifier based on a rare-earth doped polymer.

As a first step towards this goal, we report electroluminescence (EL) at 890 nm from a lissamine-functionalized terphenyl-based neodymium complex (Ls.Nd<sup>3+</sup>),<sup>4</sup> doped into poly(dioctylfluorene-alt-benzothiadiazole), F8BT. Although infrared luminescence from organic LEDs with small molecular weight emitters has already been reported,<sup>5,6</sup> we are particularly interested in the development of conjugated polymer-based active layers,<sup>8</sup> as these tend to suffer less from recrystallization problems, and are therefore more promising candidates for achieving a better diode durability.

The organic Nd<sup>3+</sup> complex used in this work was designed to shield the Nd<sup>3+</sup> ion from its environment. It also offers the possibility of binding (covalently) a highly absorbing antenna group such as lissamine, in a position close enough to the Nd<sup>3+</sup> ion to allow efficient energy transfer. We have previously shown<sup>9</sup> that after optical excitation of the lissamine sensitizer, energy is transferred very efficiently from the triplet state of the sensitizer to the Nd<sup>3+</sup> ion by a Dexter mechanism, resulting in the typical Nd<sup>3+</sup> luminescence at 890, 1060, and 1340 nm. Although we have chosen lissamine as the sensitizer, any absorbing group could be used in principle, as long as the triplet state energy of the sensitizer is resonant with one of the Nd<sup>3+</sup> energy levels.

For electrical excitation, electrons and holes should be injected in both the polymer host and the lissamine. Those charges that combine to form singlet and triplet excitons in the host can then (a) decay radiatively, or undergo (b) Förster or (c) Dexter transfer to the sensitizer; the sensitizer triplets can eventually excite the Nd<sup>3+</sup>. Note that Förster transfer is expected to be three orders of magnitude or so faster than Dexter transfer.<sup>10</sup> Some charges should also be trapped at the lissamine (owing to the lower energy gap), and later combine with oppositely charged species to form singlets and triplets.

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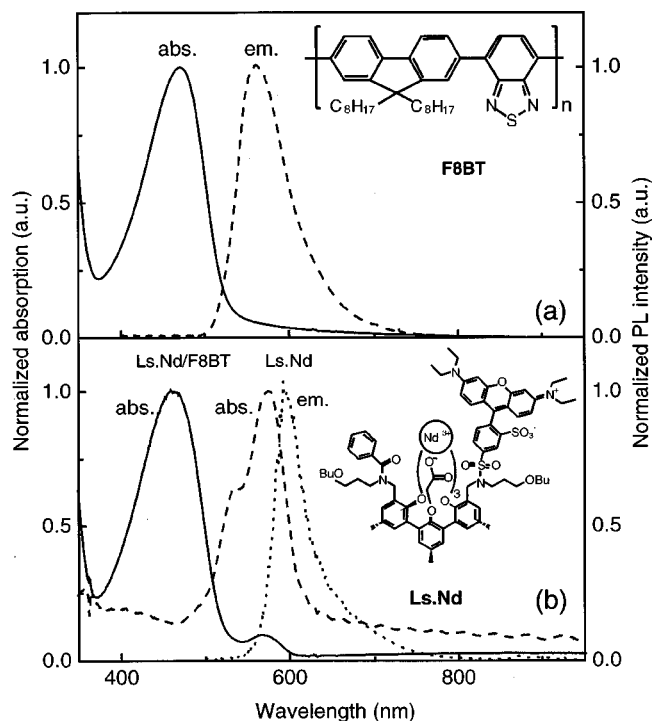


FIG. 1. Absorption and photoluminescence emission spectra together with the chemical structures of F8BT (a), and of Ls.Nd<sup>3+</sup> (b). An absorption spectrum of the Ls.Nd<sup>3+</sup>/F8BT blend is also shown.

Our results show that the luminescence of the polymeric host (F8BT) is efficiently quenched by the Ls.Nd<sup>3+</sup> complex, and that emission takes place both from the sensitizer and the Nd<sup>3+</sup>. Current–voltage and luminance–voltage curves provide indications that the lissamine acts as a charge trapping site. Charge transfer from the lissamine to Nd<sup>3+</sup> followed by direct formation of triplets on the rare earth is possible, but unlikely, due to poor stability of Nd<sup>2+</sup> and Nd<sup>4+</sup>.

Lissamine-functionalized organic neodymium complexes (Ls.Nd<sup>3+</sup>) were synthesized using the procedure described in Ref. 4, whereas Ls.Nd<sup>3+</sup>-doped LEDs were fabricated as follows. First, an indium–tin–oxide (ITO) coated glass substrate was treated with an oxygen plasma and then spin-coated with a ~40 nm thick hole injection layer of poly(3,4-ethylene dioxythiophene) (PEDOT) doped with poly(styrene sulfonate) (PSS, from Bayer). After spin-coating, the film was heated for 1 h at 100 °C under N<sub>2</sub> flow. Both the oxygen plasma treatment and the PEDOT/PSS layer serve to increase the work function of the anode,<sup>11,12</sup> and therefore reduce the energy barrier for injection of holes into the emissive layer. The emissive layer was prepared using a solution of 3.3 mg Ls.Nd<sup>3+</sup> and 35.3 mg poly(dioctylfluorene-alt-benzothiadiazole) (F8BT) dissolved in 5 ml of chloroform (chemical structures of the materials are shown in Fig. 1). This solution of 10 wt% Ls.Nd<sup>3+</sup>/F8BT blend was spin-coated onto the PEDOT/PSS layer at a spin rate of 1400 rpm, resulting in an ~80 nm thick film. Finally Ca/Al counter electrodes (area ~2 mm<sup>2</sup>) were thermally evaporated at a background pressure of ~5 × 10<sup>-6</sup> mbar.

Devices were transported under nitrogen and characterization was performed at ~10<sup>-2</sup> mbar in order to prevent oxidation of the Ca cathodes. Details about the characteriza-

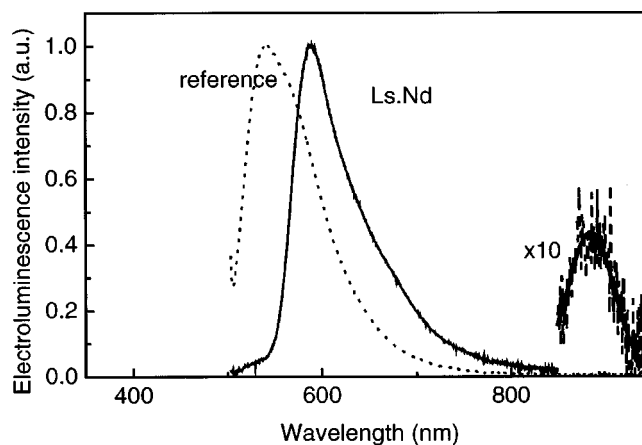


FIG. 2. EL spectrum of an ITO/PEDOT/F8BT:Ls.Nd<sup>3+</sup>/Ca/Al structure, biased at 31 V (~100 mA/cm<sup>2</sup>) (solid line). The Nd<sup>3+</sup> signal around 890 nm has been multiplied by a factor 10. The noise is related to the low detector sensitivity in the near infrared. An EL spectrum from an ITO/PEDOT/F8BT/Ca/Al reference structure without the lissamine sensitizer, biased at 6 V (~1000 mA/cm<sup>2</sup>), is also shown (dotted line).

tion of the optical and electrical properties can be found in Ref. 11.

Photoluminescence reference measurements were performed on Ls.Nd<sup>3+</sup> doped polycarbonate wave guides as described in Ref. 9, using the 458 nm line of an Ar ion laser at a power density of 2 W/cm<sup>2</sup> for excitation. Optical absorption measurements were performed at normal incidence.

F8BT was chosen as the host material because it has a very high PL efficiency in the solid state (~0.6) along with good solubility in common organic solvents, and a high electron affinity (~2.9 eV), which facilitates electron injection from common cathodes, such as Ca. Figure 1(a) shows the absorption and photoluminescence spectra of undoped F8BT. Figure 1(b) shows the absorption spectra of Ls.Nd<sup>3+</sup> in a polymer film and of the Ls.Nd<sup>3+</sup>/F8BT blend. The latter shows contributions from F8BT and Ls.Nd<sup>3+</sup>. Note that there is considerable overlap between the emission spectrum of F8BT and the absorption spectrum of Ls.Nd<sup>3+</sup>, which allows efficient Förster energy transfer from the conjugated polymer to the Ls.Nd<sup>3+</sup> complex.

Figure 2 displays the EL spectrum of the Ls.Nd<sup>3+</sup> doped LED (solid line). The luminescence around 600 nm originates from the lissamine sensitizer. Emission at ~890 nm from the Nd<sup>3+</sup> ions is also clearly detected, whereas emission from the F8BT is not. The integrated 890 nm emission intensity of Nd<sup>3+</sup> amounts to ~3% of the total intensity. The Nd<sup>3+</sup> luminescence at 890, 1060, and 1340 nm results from transitions between the <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>9/2</sub>, <sup>4</sup>I<sub>11/2</sub>, and <sup>4</sup>I<sub>13/2</sub> levels, and thus stems from the same luminescence level. All three transitions have been observed previously for the Nd<sup>3+</sup> complexes in a polycarbonate film. It is assumed that the polymer matrix does not have a large effect on the branching ratios of the transitions within the Nd<sup>3+</sup> ion, as the ion is shielded from the polymer by the complex. Typical integrated intensity ratios of the Nd<sup>3+</sup> luminescence are 12:14:3 (890 nm:1060 nm:1340 nm) as measured on Ls.Nd<sup>3+</sup> doped polycarbonate waveguides.<sup>9</sup> Using these intensity ratios, and the estimated Nd<sup>3+</sup> luminescence quantum efficiency of 1%, it can be estimated that the majority of the excitation on the sensitizer is transferred to the Nd<sup>3+</sup> ion.

Although the lissamine luminescence is undesired for near-infrared applications, it provides a convenient visible probe of singlet exciton formation and recombination. The incomplete quenching of the lissamine luminescence is evidence that intersystem crossing (ISC), i.e., singlet-triplet transfer within the lissamine, is not efficient in competing with radiative decay of the lissamine singlet state ( $\eta_{isc} \sim 60\%$ ).<sup>4</sup> This also implies that there is considerable scope for improvement. In fact, we are currently developing materials and devices aimed at achieving complete quenching of the sensitizer luminescence via optimized ISC and different bonding configurations between sensitizer and complex. This should reduce the distance between the sensitizer and the rare-earth emitter and improve the energy transfer. The possibility of using both singlet and triplet emission may in principle allow an EL quantum efficiency close to 100%.<sup>13</sup>

When measured relative to the lissamine emission, the  $\text{Nd}^{3+}$  emission around 890 nm is about 4 times higher than in PL experiments on  $\text{Nd}^{3+}$ -doped polycarbonate waveguides [see dashed line in Fig. 1(b)]. Note that in PL experiments the optical excitation generates singlet excitons, whereas for EL we expect a larger proportion of triplet states to be formed on both the F8BT and on the lissamine, owing to the fact that charge injection is not spin polarized. The measured ratio between the 890 nm emission in EL and PL indicates that the relative triplet population on the lissamine is higher in EL than in PL. It is difficult to provide an accurate estimate of the fraction of triplets which have diffused via Dexter transfer from F8BT, but we note that this will strongly depend on the relative values of the Dexter transfer rate (typically three orders of magnitude or so slower than singlet transfer rates),<sup>10</sup> of the lissamine ISC rate (that we know to compete quite efficiently with fluorescence;  $k_{ISC} = 4.4 \times 10^8 \text{ s}^{-1}$  and  $k_{\text{fluor-ligand}} = 3.8 \times 10^8 \text{ s}^{-1}$ ),<sup>4</sup> and of the rate of direct triplet generation onto the lissamine. However, we note that  $\text{Nd}^{3+}$  emission intensity is essentially comparable with lissamine electroluminescence, and that the first two mechanisms appear unlikely to be able to sustain such a fast exciton delivery to the lissamine triplet level, whereas direct triplet generation following charge trapping should be directly linked to the rate of singlets generation. We consider therefore that the majority of triplets is directly generated onto the lissamine, following charge trapping (see also Fig. 3).

Figure 2 also shows the EL spectrum of a reference device doped with a  $\text{Nd}^{3+}$  complex without the lissamine<sup>7</sup> (dotted line). This shows clear luminescence from the F8BT, but no  $\text{Nd}^{3+}$ -related emission, proving the crucial role of the lissamine.

Figure 3 displays the current and luminance versus voltage characteristics for the  $\text{Ls.Nd}^{3+}$  doped LED. The turn-on voltage for visible emission  $V_{on}$  (at  $0.01 \text{ cd/m}^2$ ) is  $\sim 15 \text{ V}$ , which is relatively high compared to that of pure F8BT structures ( $2.5 \text{ V}$  or less). This has to be related to the low efficiency which is  $\sim 8 \text{ mcd/A}$  as can be seen in the inset of Fig. 3. Even though the low PL efficiency of the lissamine (which is measured to be 3%–7% depending on deposition conditions) might be expected to increase the threshold, we

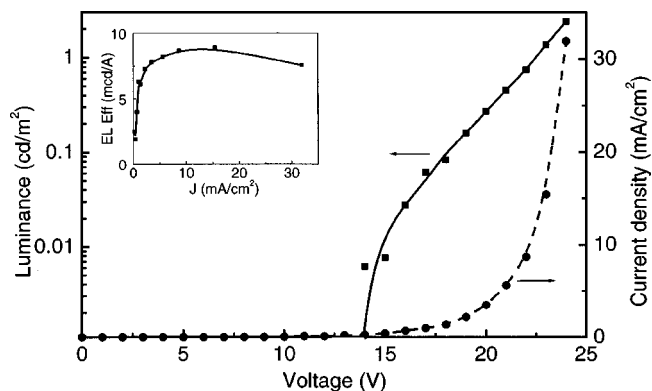


FIG. 3. Current–voltage (closed circles) and luminance–voltage (squares) characteristics for an ITO/PEDOT/F8BT:Ls.Nd<sup>3+</sup>/Ca/Al LED structure. Active area is  $\sim 2 \text{ mm}^2$ , thickness of the active layer is  $\sim 80 \text{ nm}$ . The inset shows the efficiency in the visible, i.e., due to the lissamine (luminance/current), as a function of the current density through the device.

notice that the voltage dependence of the luminance is very steep close to the turn on. We consider that this is an indication that the  $\text{Ls.Nd}^{3+}$  complex acts as a trap and reduces electron and/or hole mobilities with respect to those of pure F8BT. A similar increase of turn-on voltage has been observed for sensitized visible-emitting lanthanide complexes doped into conjugated polymers.<sup>14</sup>

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